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DESIGN OF ANALYTICAL SYSTEMS FOR QUANTITATIVE MEASUREMENT OF HAZARDOUS SUBSTANCES IN AIR, WATER AND SEDIMENTS

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DESIGN OF ANALYTICAL SYSTEMS FOR QUANTITATIVE MEASUREMENT OF HAZARDOUS SUBSTANCES IN AIR, WATER AND SEDIMENTS

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DESIGN OF ANALYTICAL SYSTEMS FOR QUANTITATIVE MEASUREMENT OF HAZARDOUS SUBSTANCES IN AIR, WATER AND SEDIMENTS

AND

CALIBRATION OF THE HNU PHOTOANALYZER FOR DETECTING HAZARDOUS SUBSTANCES

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1. INTRODUCTION

1.1 General

These studies were proposed by the Environmental Emergency Branch (EEB) of the Environmental Protection Service (EPS). The proposals were based, to a considerable extent, on a study carried out for EEB in 1980-81, and reported on April 2, 1981 under the title of "The Design of an Analytical System for the Detection and Monitoring of a Number of Hazardous Materials". The study was carried out by the Principal and Co-Investigators responsible for this present Report.

The 1980-81 study made recommendations concerning equipment felt to be suitable for the detection and monitoring of a number of hazardous materials, and these recommendations cited specific testing tubes (Drager), field testing kits (HACH, HMDK and/or DR-EL/4), field gas chromatographic (GC) units (OVA) and detection units (HNU), microprocessed UV and IR spectrophotometers (P-E Model 552 UV;P-E Model 683 IR) and on-line computer linkage for the UV and IR units with possible extension to a laboratory-style GC unit (Radio Shack TRS 80, Mark III computer). The present proposal was intended to carry out experimental work on these units, as purchased and supplied to the project by EEB, in order to determine their ability to provide quantitative responses to a number of hazardous substances.

The general objective of the study was to provide systems able to detect, identify and quantify hazardous sub-

stances at spill sites. The systems were to be operative relative to air, water or sediment/soil samples. Three levels of detection/quantification were to be implemented, and these were:-

1. Level I - Drager tubes
2. Level II - HACH kits, OVA, HNU
3. Level III - Computerized IR/UV-VIS spectrophotometry

These general features of each level are indicated in the following.

1.1.1 Level I methods

Drager tubes

The objective of Level I testing is to determine relatively small concentrations of a contaminant (or contaminants group) in air samples, and to do this with maximum reliability and in minimum time. The purpose of such determinations is to indicate quickly and easily whether the contaminant(s) involved exists at a concentration above an admissable level. At spill sites, Level I testing would be expected to provide initial data concerning the concentration of a contaminant(s) in the air.

Drager tubes are designed to meet this need. There are approximately 100 different tubes available in the Drager gas detection system. As normally used, a measured amount of the air sample is drawn through the active material in the tube, whereupon a colour change reaction takes place on the solid reagent carrier. The determination of the level of the

particular contaminant involved is obtained by either matching the degree of colour change against colour/concentration standards, or by measuring the distance the colour change has travelled through the tube and comparing it with a calibrated scale.

The Drager tube system can only be applied to air samples taken at temperatures approximating 20°C. The results are semi-quantitative and, where circumstances require more accurate testing, Level II and/or Level III methods must be applied.

1.1.2 Level II methods

HACH DR-EL/4 kit

This kit, properly called the Direct Reading Engineer's Laboratory, is a self-contained, portable field kit for the quantitative determination of about 30 different substances of a hazardous nature that are commonly found in potable waters. The individual analyses are generally carried out by titrimetric or colourimetric means, although conductometric measurements can also be applied.

A number of "spot" tests can be carried out by the kit. These tests can determine whether or not a given contaminant is present at a limiting concentration, but they are not capable of being applied as a quantitative determination.

In general, a sample of the water media is tested without pretreatment, dilution or concentration steps being required.

OVA (organic vapour analyzer) Model 128, GC option

This unit is a highly-sensitive instrument designed to measure trace quantities of organic materials in air sample media. It employs what is essentially a hydrogen-flame ionization detector (FID) with sensitivities in the ppm v/v range, and can operate in the presence of moisture, oxides of nitrogen and carbon dioxide.

The unit measures organic vapour concentrations by the comparative method; the response to a sample of air of unknown contaminant concentration is compared with the response yielded when a contaminant mixture of known concentration is tested. Since the sensitivity of the FID varies from one organic vapour to another, the instrument must be calibrated for each organic compound of interest.

When the instrument is operated in the normal survey mode (sniffer mode), a continuous sample is drawn through the probe into the detector chamber by means of an internal pumping system. Within the detector, the sample is burned in the hydrogen flame, and this combustion produces positively-charged carbon-containing ions which are collected by a negatively-charged electrode in the chamber. The resulting ion current is measured and an output signal results which is proportional to the number of ions collected. The signal is amplified for subsequent display as quantitative data on the readout meter or external recorder.

In the "sniffer" mode all FID-sensitive vapours present in the air sample are measured simultaneously. Thus, if there

are two or more organic substances in the air sample under study, the OVA will give a single response proportional to the total concentration of the organic vapours present.

If it is necessary to separate and quantify the individual components of the sample, the OVA must be operated in the "GC" mode. In this mode of operation, the sample is injected into the GC column. The components are separated and eluted individually into the detector chamber where each FID response is measured. Qualitative analysis is based on the retention times for the various components, with quantitative data being obtained by the measurement of the individual peak areas (triangulation) of the recorder chart. Comparison with known standards is required.

HNU PI-101 (photoionization detection system)

The HNU is a UV photoionization detector system capable of determining in air samples those organic vapours as contaminants which are sensitive to photoionization detection at 10.2 eV. Since the response varies from one organic substance to another, the HNU must be calibrated for each compound of interest. Mixtures of organic substances which are each sensitive to photoionization detection, will provide for a total response.

Qualification is not possible, nor is quantification possible except in the analysis of air samples containing only one photoionization sensitive substance. This is, in itself, not necessarily severely restrictive, since many spill incidents

involve situations where only one organic contaminant substance of a hazardous nature be quantified.

1.1.3 Level III methods

UV/IR computer-linked methods

The microprocessed UV and IR units, linked to the on-line computer, are capable of providing for the quantification of many organic vapours representing hazardous contaminants in air samples. Qualification and quantification are possible and, with restrictions, air samples containing more than one contaminant can be investigated. In a manner similar to that involving the use of head-space sampling techniques in GC work, water and soil/sediment samples can also be analyzed.

Very generally, the operational principle involves logging into the computer banks the UV and/or IR data involving, for example, wavelength, extinction coefficient, calibration data, etc., for each organic compound of interest and responsive to UV and/or IR spectroscopic examination techniques. Recall of this information involving operational settings for any logged compound and the subsequent introduction of the sample to be analyzed results in the provision of ratio data covering the response factor for the unknown and the response factor/concentration from logged standard-samples information. From this ratio data, the concentration of the contaminating analyte in the air sample can be obtained by simple calculation.

1.2 Priorities for Hazardous Substances and Test Media

1.2.1 Priority lists for hazardous substances

The lists for priority hazardous substances, as stipulated by EEB for this study, are shown in Appendix A. The 1980-81 study had suggested (Section 2.1) priority listings for hazardous substances normally shipped in gas, liquid or solid form. The groupings shown were arranged as to priorities on the basis of:

(a) Ability to contaminate the air

(b) Ability to contaminate water or soil/sediment

(c) Degree of danger to human health

(d) Probability of a spill based very generally on the frequency/quantity of shipments

(e) Possibility of additional hazard in the event of fire

The compounds stipulated by EEB as priority hazardous substances are listed in fair agreement with these suggestions.

1.2.2 Priority of test media

In general the order of importance relative to the test media was established as:

1. Hazardous substances in air media
2. Hazardous substances in water media
3. Hazardous substances in soil/sediment media

The test procedures are fairly simple for air media

work, but can become somewhat more complicated with respect to the testing of water and soil/sediment samples. These latter two media require that consideration be given to the methodologies of sampling and introduction of the samples acquired to the particular testing equipment involved (e.g. GC, UV or IR).

1.2.3 Priority of analytical location

Acquired samples of any media can be tested in the field (at the spill site), at portable test areas (equipment located in a carrier nearby) or in a fixed laboratory (this could be in a well-designed carrier nearby or in a base laboratory). It is at once apparent that the order of importance is exactly the line-up as shown; namely that the descending order of priority is field testing, portable testing and laboratory testing. The need for, first of all, rapid and accurate field testing techniques is paramount, and it is towards this area that the initial experimental work was directed.

1.3 Progress of the Experimental Investigations

It had been initially anticipated that the various systems of analysis, except possibly that involving computer-linked UV/VIS and IR spectrophotometry, would be completely explored and documented before the terminal date of March 31, 1982 for both Contracts. Although the Drager tube work and most of the HACH kit studies were completed well

before this date, continual equipment breakdowns, delays in obtaining equipment from the manufacturers and their Canadian agents, delays in having instruments returned from the manufacturers after repair, missing parts and problems arising out of the techniques developed for the preparation and sampling of calibration standards all plagued the OVA and HNU programs.

The following provides a more detailed but considerably shortened picture of these unfortunate events.

1.3.1 OVA delivery and operational problems

Appendix B gives a very general idea of the nature of the problems encountered relative to the OVA unit and its accessories. These represent only a fraction of the difficulties which arose. The Foxboro organization were excellent to deal with on the telephone with respect to the discussion of operational problems and the obtaining of associated advice. They were less easy to deal with where it became essential to get units repaired and returned, and to supply lost or nonfunctional parts replacement. The Canadian agent was of little help in expediting delivery of new or repaired instruments.

It should not be taken from the foregoing that the OVA unit is not suited or not adaptable to field application in quantifying hazardous substances at spill sites. We have, indeed, found that, with the initial operational problems corrected, the unit shows considerable promise from the

points of view of precision, accuracy and sensitivity.

The continuous delays caused by the necessity of working out the kinks in instrument operation were exceedingly frustrating and, of course, resulted in this section of the exploratory program being incomplete at the terminal date of the Contract.

At the present moment, the OVA work in connection with the extension of the Contract into the 1982-83 Contract, is progressing very well indeed, and will be terminated well before the period of January, 1983.

1.3.2 HNU operational problems

Appendix B again provides a few examples of the problems encountered in connection with this equipment. Here again we feel that the HNU will be satisfactory for field use in its area of applicability. Experimental work in this connection is proceeding rapidly at the moment in connection with the 1982-83 Contract. It is anticipated that all testing work will be completed by December, 1982-January, 1983.

1.3.3 Perkin-Elmer computer-linked UV/IR problems

Operational difficulties were experienced only with respect to the UV-VIS microprocessed spectrophotometer, Model 552A. The nature of this problem is outlined in Appendix B. Some 45 days delay resulted from this situation.

Due to the complexity of the problem surrounding the establishment of methodologies for computer linkage in a

manner such that the simplest possible mode of operation and analysis data readout would be available, this program lagged quite seriously until about January-February, 1982. The methodologies are now well-established, and the process of applying the equipment to standard samples for calibration purposes is well underway. Completion is expected in the neighbourhood of January-February, 1983.

1.3.4 Problems surrounding the preparation of calibration gas samples for standardization purposes

It was originally felt that the use of green plastic garbage bags on a once-only basis would suffice as a means of preparing standard gas mixture samples for all calibration purposes. This procedure was suggested by the OVA Manual. The general procedure and its attendant difficulties are explained in the Section on experimental work involving the OVA. It is enough to state at the moment that problems were encountered on the basis of reaction/absorbance phenomena when these bags were used with many of the hazardous substances requiring investigation. Eventually, on November 13, 1981 it was found necessary to order 20 aluminized polyester (Mylar) sample bags. Due to an error in the ordering procedure, only one bag was received on March 1, 1982. On March 10, 1982 the remaining 19 bags were received.

This situation resulted in a significant delay in approaching the final experimental steps, although the methodologies developed for gas sample preparation using the

garbage bag technique proved entirely satisfactory in the long run when the polyester bags became available.

1.3.5 Preparation of operational manuals for training courses

Although these manuals are at this moment well along in the preparation stages, their starting periods were continuously delayed over the period of the 1981-82 Contract. These delays were, of course, due to the operational and delivery problems outlined in Sections 1.3.1 to 1.3.4 inclusive.

1.3.6 Conclusions

The various difficulties which delayed the completion of the program laid out for the 1981-82 Contract can be considered as "teething" problems to be expected in the adaptation to field and portable testing conditions of the instruments involved. In the continuation of this study into the 1982-83 Contract, the exploratory work is proceeding very well indeed, and this has occurred largely on the basis of the learning process arising out of previous operational difficulties and their various solutions. No little credit should be given as well to the accumulation of experience on the part of the investigators. No problems are foreseen, at the moment, with respect to completion of the project, the training manuals and the training programs before the March 13, 1983 termination date for the 1982-83 Contract.

2. EXPLORATORY WORK FOR LEVELS I AND II SYSTEMS

2.1 Drager Tube Usage Investigation - Level I

2.1.1 General

Although some 100 Drager tubes are available for the testing of the presence of contaminants in the air, it was not felt necessary to run tests on all of these. The main point at issue was to check sufficient tubes of various types in order to obtain a general feeling for the ability of these units to function as early-warning systems to detect semi-quantitatively the presence in the air at spill sites of significant concentrations of the various hazardous substances. To this end approximately 20 different Drager tube types were tested, and these were as indicated in Table 2-1. All tests were carried out on prepared standards at concentration levels agreeing with the indicated tube range.

The method of testing is simple. The selected detection tube is readied for use by breaking the ends of the glass tube and inserting the tube into the bellows pump. Operation of the pump draws the air sample through the active ingredient in the tube body. Instructions specific to each tube type are given in the instruction data sheet accompanying the detector tube being used. These instructions also provide information concerning the number of bellows strokes required, the colour change to be expected, the concentration range detectable and the method to be used to obtain semi-quantitative data concerning the concentration of the hazardous

TABLE 2-1

DRAGER TUBES TESTED IN EXPLORATORY PROGRAM*

Substance	Tube No.	Conc. range (ppm)
Acetone	100/b	100 - 1200
Benzine-hydrocarbons	100/a	100 - 2500
Acetic acid	5/a	5 - 80
Carbon disulphide	0.04	13 - 288
Acrylonitrile	51/a	5 - 30
Aniline	5/a	2 - 10
Benzene	5/a	2 - 40
Sulphur dioxide	1/a	1 - 25
Hydrogen sulphide	1/c	1 - 200
Vinyl chloride	0.5/a	0.25 - 6
Ammonia	5/a	5 - 700
Trichloroethylene	10/a	10 - 500
Carbon monoxide	5/c	5 - 700
Nitrous fumes	0.5/a ($NO + NO_2$)	0.5 - 10
Chlorine	0.2/a	0.2 - 30
Acetaldehyde	100/a	100 - 1000

*Tests generally run against standards and checked against OVA/HNU data.

substance.

2.1.2 Results obtained from the testing program

Colour changes

It was observed that all tubes embodying pale colour shifts such as colourless to pale pink, pale yellow, pale blue, etc., were difficult to evaluate, or even to detect properly, except in a bright light.

Bellows pump problems

The bellows pump is sensitive to temperature and operates poorly at temperatures of 10°C and lower. This was confirmed by tests carried out in a solvent storage room kept at 5°-10°C. This situation is important but, in view of the fact that a temperature of about 20°C (see Section 1.1.1) is required to yield a dependable colour-change reaction, it is not by itself overly significant.

Bellows pump strokes

It was frequently found that the standard sample required more bellows pump strokes to produce the expected colour change than was recommended on the associated instruction sheet. Correspondingly, these required strokes must be repeated in number for the unknown.

It was found that there was, generally speaking, too much dependency on the speed of compressing and releasing the bellows of the pump, and that variable speeds resulted in

different volumes passed through the active ingredient in the tube.

Test tube breaks

It was found that the tubes do not always break with a constant orifice size. It is the feeling of the investigating body that this can lead to variable air sample volume, even with carefully controlled bellows pump operation and stroke number. A variable air sample volume could lead to spurious concentration readings.

Semi-quantification

Leaving aside all of the problems indicated in the foregoing, the tubes reported the standard value with some semblance of conformity to the indicated range value, although the degree of conformity spread itself rather badly over the range.

Shelf life

Many of the tubes have a restricted shelf-life, and should very definitely not be used when this has been exceeded.

2.1.3 Conclusions

The Drager tubes can be used to provide a very crude first indication of the concentration of a hazardous substance in the air at a spill site. The investigators would highly recommend that any such preliminary indication be supported immediately with a second set of tests employing instruments

capable of providing precise and accurate reporting. In no way should any important decisions be taken at spill sites, such as choice or rejection of protective clothing, area evacuation, etc., on the basis of Drager tube tests alone.

2.2 HACH DR-EL/4 Kit Investigation - Level II

2.2.1 General

In order to check out the ability of the HACH DR-EL/4 kit to provide a satisfactory analysis scheme for water samples, nearly all of the water analysis procedures outlined in the DR-EL/4 Manual were investigated on a practical basis. In addition, tests were carried out to determine the performance characteristics of the Digital pH Meter, glass electrode and temperature probe assembly provided with the HACH kit.

During all of the test procedures, the test details were carried out in accordance with the instructions outlined in the DR-EL/4 Manual. Where departures were required, these have been noted in a commentary at the end of each test description. Standard solutions were prepared and used as "unknowns" to determine the general orders of precision/accuracy for each technique. Notes were carefully taken for each procedure and, in a section at the end of each test description, important features of correction or recommendation are set out.

2.2.2 Specific test procedures

2.2.2.1 HACH digital pH meter, electrode and temperature probe tests

On page 2-47 of the DR-EL/4 a methodology is described which covers the determination of the pH of water and waste water samples by the glass electrode/pH meter technique. This test procedure is intended to indicate the acidity or alkalinity of samples of water or waste water.

While carrying out the required tests on various buffer solutions used for both calibration and pH determination purposes, the data from the HACH test assembly were compared with those from a "Concordia" pH meter assembly and a Metrohm 300B pH meter assembly. Table 2-2 shows the data obtained.

All units were calibrated in the manner recommended for the HACH assembly, regardless of the individual instructions. On this basis, it will be noted that the pH differences between the buffer values and the values read off the equipment are larger for the Metrohm 300B unit than for the HACH or "Concordia" units, and that this is particularly the case where the tests are made under quiescent solution conditions. This can be attributed to the fact that the calibration procedure for the 300B differs somewhat from that applied, as well as to the fact that the electrode system responds well only under stirred solution conditions. In making all comparisons, therefore, stirred solution data should be given particular emphasis.

TABLE 2-2

COMPARISON OF THE HACH DIGITAL pH METER AND ELECTRODE/ TEMPERATURE PROBE ASSEMBLY WITH "CONCORDIA" AND METROHM 300B ASSEMBLIES

All units: calibrate at 4 and 9 pH with appropriate buffers

All tests: (a) quiescent solution conditions
(b) Magnetically-stirred solution conditions

Test sample	Test time lapse (m)	HACH digital pH meter (a)	HACH digital pH meter (b)	Metrohm 300B pH meter (a)	Metrohm 300B pH meter (b)	"Concordia" pH meter (a)	"Concordia" pH meter (b)
4.00	0.5	4.07	4.01	3.82	4.00	3.99	4.00
	1	4.05	4.01	3.76	3.98	3.98	3.99
	2	4.04	4.01	3.68	3.98	3.97	3.98
	5	4.04	4.01	3.68	3.98	3.96	3.96
	10	4.02	4.01	3.68	3.98	3.95	3.93
7.00	0.5	7.17	7.10	6.48	6.82	6.93	6.96
	1	7.12	7.10	6.48	6.82	6.95	6.95
	2	7.11	7.10	6.52	6.82	6.95	6.95
	5	7.10	7.10	6.52	6.82	6.96	6.95
	10	7.09	7.10	6.50	6.82	6.97	6.94
9.00	0.5	9.00	9.07	8.28	8.80	8.90	8.84
	1	9.00	9.06	8.38	8.82	8.89	8.83
	2	9.00	9.07	8.43	8.82	8.88	8.83
	5	8.99	9.06	8.48	8.80	8.88	8.83
	10	8.98	9.06	8.42	8.75	8.88	8.83
10.00	0.5	10.06	10.13	9.19	9.70	9.91	9.90
	1	10.05	10.13	9.32	9.87	9.94	9.91
	2	10.04	10.13	9.45	9.85	9.94	9.91
	5	10.04	10.13	9.48	9.85	9.95	9.91
	10	10.03	10.12	9.48	9.85	9.95	9.91

The HACH assembly showed excellent stability and yielded valid results for the buffer solutions tested. Sufficient time must be allowed to attain an equilibrated position, and it was found that 2 minutes should suffice for this purpose.

Although the HACH assembly showed minimal differences between the quiescent and stirred solution readings, it is very definitely recommended that stirring should be applied at all times. The following general conclusions were drawn:

Conclusions

1. The HACH Digital pH Meter and electrode/probe assembly is a sensitive and accurate device for the determination of the pH of waters and waste waters. pH values would generally tend to be between 4 and 9, with values outside this range being indicative of serious intrusion into the sampled water of acid or alkaline substances.

2. At least one extra glass electrode assembly and one extra temperature probe should be carried out at all times.

3. Shaking or hand-stirring of solutions to be tested during pH estimation can result in electrode breakage, even with the protected HACH electrode. In any case, hand-stirring is not as reliable in yielding fast equilibration as magnetic stirring. On this basis, it is recommended that a small magnetic stirring/heater plate, with a sufficient supply of stirring bars, be carried out with the equipment. In the event that 115V ac power is not available at the

site or from the site van, an ac converter from a dc battery, or a battery-operated unit, should be available.

2.2.2.2 Acidity - free and total

This test is supposed to determine the acidity of waters or waste waters by titration techniques involving 1.589N NaOH standard solution and a digital readout hand burette. "Free" acidity expresses the quantity of strong mineral acids, and is determined by titration with a bromophenol blue indicator. "Total" acidity is expressed as "free" acidity plus weak acids such as carbonic acid and organic acids. The method involves heated sample solution titration to a phenolphthalein endpoint. In each case, the acidity value is read off the digital burette in terms of ppm equivalent of $CaCO_3$.

Only the "total" acidity was determined in the investigation procedures, and this was determined against standard solutions prepared using hydrochloric, sulphuric, nitric, phosphoric and acetic acids. Table 2-3 shows the data obtained. The experimental details followed were those outlined on pages 2-3 and 2-4 of the DR-EL/4 Manual.

It will be noted that, in general, good agreement was found between the test values and the appropriate standard solution values. The sulphuric acid solution standard showed a somewhat low value, but this was not felt to be overly significant.

TABLE 2-3

"TOTAL" ACIDITY DETERMINATION - DR-EL/4 MANUAL, PAGES 2-3 AND 2-4

Acid	Standard strength (ppm $CaCO_3$ equiv)	"Total" acid value (ppm $CaCO_3$ equiv)
Hydrochloric, HCl	250	249
Sulphuric, H_2SO_4	250	210
Phosphoric, H_3PO_4	167	176
Nitric, HNO_3	250	259
Acetic, $CH_3 \cdot COOH$	250	230

Available range: 0 - 250 ppm acidity as $CaCO_3$

Conclusions

1. The test for "total" acidity provided results indicating that the HACH DR-EL/4 test method provides satisfactory results.
2. The need for a magnetic stirrer/heater plate is confirmed (see "Conclusions", Section 2.2.2.1).
3. For this test, and for others in the DR-EL/4 Manual, demineralized water is often required. A quantity of demineralized water of not less than five gallons should be maintained in reserve at all times.
4. A pipetting bulb should be carried out for use with pipettes measuring samples or methodology reagent solutions.
5. Although the kit contains, at the inception, a reasonable supply of Buffer Powder Pillows, NaOH reagent, etc., a large home-base supply of all consumable reagents and solutions should be maintained.

2.2.2.3 Alkalinity - P and T

These tests are designed to indicate the alkalinity of samples of water and waste water. The methodologies are outlined in the DR-EL/4 manual pages 2-5 to 2-7. The "P" alkalinity is expressed as the phenolphthalein alkalinity, is determined by titration to a phenolphthalein endpoint using 1.589N H_2SO_4 solution and represents the total hydroxide plus one-half of the carbonate present. The "T" alkalinity is

expressed as the total alkalinity, is determined by continued titration beyond the phenolphthalein endpoint to a bromo-cresol green/methyl red endpoint, and expresses the total of the hydroxide, carbonate and bicarbonate alkalinities.

Tests were carried out using standard solutions involving sodium hydroxide and sodium carbonate. The results obtained are shown in Table 2-4.

It is apparent that the standard NaOH solution prepared contained an appreciable amount of sodium carbonate, the result of the reaction of NaOH with atmospheric CO_2. No attempt had been made, when preparing the NaOH solution, to provide protection against the absorption of CO_2.

The results obtained showed good agreement, insofar as comparisons could be made, with the standard solutions.

Conclusions

1. The test procedures for P and T alkalinities in the HACH DR-EL/4 Manual provided results indicating a satisfactory situation.
2. The need for an adequate reserves of demineralized water and a large home-base supply of expendable solutions and reagents is confirmed (see "Conclusions", Section 2.2.2.2).

2.2.2.4 Calcium hardness of waters

This test, pages 2-10 and 2-11 of the DR-EL/4 Manual, is intended to determine the calcium hardness of water and waste water samples. The magnesium hardness can be determined

TABLE 2-4

ALKALINITY DETERMINATIONS - DR-EL/4 MANUAL, PAGES 2-5 TO 2-7

	Standard strength (ppm $CaCO_3$ equiv)			Alkalinity value (ppm $CaCO_3$ equiv)		
Alkali	OH^-	$CO_3^=$	HCO_3^-	OH^-	$CO_3^=$	HCO_3^-
(1) sodium hydroxide	(274) 800	not added	not added	(252) 741	74	0
(2) sodium carbonate	not added	250	not added	3	256	0

(1) P = 774 ppm T = 815 ppm

OH^- = (2xP) - T = 741 ppm $CaCO_3$ equivalent

$CO_3^=$ = (T - P) x 2 = 74 ppm $CaCO_3$ equivalent

HCO_3^- = 0

(2) P = 128 ppm T = 253 ppm

OH^- = (2xP) - T = 3 ppm $CaCO_3$ equivalent

$CO_3^=$ = 2 x P = 256 ppm $CaCO_3$ equivalent

HCO_3^- = 0

Available range: 0 - 250 ppm alkalinity as $CaCO_3$

by subtracting the calcium hardness from the total hardness as determined on pages 2-31 and 2-32 of DR-EL/4.

The methodology for the calcium hardness determination involves titration of the sample with 0.794M EDTA solution, using 8N KOH solution to provide the necessary solution alkalinity and CalVer 2 indicator for the endpoint location. The digital readout burette provides the titration information as ppm $CaCO_3$ directly in the water sample.

Magnesium must be present in order for this titration to be carried out properly, although magnesium is not determined in the titration procedure. Natural waters will usually contain sufficient magnesium. Where there is any doubt as to its presence, it must be added to the water sample before titration in the form of one or two drops of 10,000 ppm Mg^{2+} solution ($MgCl_2 \cdot 6H_2O$ is normally used for preparation of this solution).

In the test situation applied, standard solutions were prepared from calcium carbonate, calcium hydrogen phosphate and calcium chloride. The results obtained are shown in Table 2-5.

It will be noted that, with the exception of the standard prepared using calcium hydrogen phosphate, the various prepared solutions analyzed very satisfactorily. The problem encountered with the calcium hydrogen phosphate standard arose out of the precipitation of calcium phosphate during the pH increase brought about by the addition of 8N KOH.

TABLE 2-5

CALCIUM HARDNESS DETERMINATION - DR-EL/4 MANUAL, PAGES 2-10 AND 2-11

Calcium salt	Standard strength (ppm $CaCO_3$ equiv)	Hardness value (ppm $CaCO_3$ equiv)
Calcium carbonate, $CaCO_3$	1000.3	1009.0
	800.3	806.0
	500.2	494.0
	200.1	200.5
Calcium hydrogen phosphate, $CaHPO_4$	1000.0	variable
Calcium chloride, $CaCl_2$	902.0	910.0

Available range: 0 - 1000 ppm $CaCO_3$ calcium

Conclusions

1. The DR-EL/4 method for the determination of calcium hardness yields excellent results. Solutions containing compounds of calcium cannot be analyzed with any accuracy.
2. Care must be taken in handling the 8N KOH solution, due to its serious attack on skin and the eyes.
3. Where transition and heavy metals of certain types are present complexiметric interference with the indicator reaction may require the pre-titration addition of KCN. Extreme care must be taken in handling and storing this reagent. There must be no departure from the indicated order of making the KCN addition.
4. Adequate home-base stocks of all expendable reagents and solutions must be maintained.

2.2.2.5 Chloride in waters

The method is covered in the DR-EL/4 Manual, pages 2-14 and 2-15. The technique determines chloride in water samples by titration with 2.256N mercuric nitrate solution. A digital readout titrator is used which yields the titration value of chloride directly as ppm. Diphenylcarbazone is used as the endpoint indicator.

Chromate, ferric iron, sulphide and sulphite can interfere. Iodide and bromide interfere directly, and are reported as chloride. Sulphide interference can be prevented by the pre-titration addition of Sulphide Inhibitor Pillows. Sulphite

interference can be prevented by the pre-titration addition of 30 percent hydrogen peroxide.

Standard solutions of chloride ion were prepared using sodium, potassium, ammonium, zinc and calcium chlorides. A solution was also prepared using hydrochloric acid. Table 2-6 shows the results obtained.

The data indicated shows test results that were quite satisfactory, although a tendency to yield high results was noted for waters or solutions of relatively low chloride content (e.g. less than 30 ppm). This is likely due to the fact that there is no indicator blank correction applied. The colour change involves a first very faint pink that is not always easily to ascertain.

Conclusions

1. The DR-EL/4 method for chloride determination in water and waste water samples yields satisfactory results. With low concentration samples (less than about 30 ppm) some tendency exists for high values to be obtained.
2. Adequate supplies of all expendable reagents, solutions and inhibitors must be available on-site and in home-base storage.

2.2.2.6 Total chlorine in waters

This test, covered by the DR-EL/4 Manual, pages 2-16 and 2-17, covers the determination of the total chlorine content of waters and waste waters. The method involves the use of

TABLE 2-6

CHLORIDE DETERMINATION - DR-EL/4 MANUAL, PAGES 2-14 AND 2-15

Chloride salt	Standard strength (ppm Cl equiv)	Test value (ppm Cl equiv)
Sodium chloride, NaCl	76.2	78.0
	61.0	66.0
	30.5	36.0
	6.1	9.5
Potassium chloride, KCl	125.0	120.0
Ammonium chloride, NH_4Cl	101.4	104.0
Zinc chloride, $ZnCl_2$	125.0	127.5
	250.0	240.0
Hydrochloric acid, HCl	125.0	125.0
Calcium chloride, $CaCl_2$	125.0	132.0

Available range: 0 - 125 ppm chloride

N,N-diethyl-p-phenylenediamine as an addition to the water sample. A red colour is developed if chlorine is present. The intensity of the colour is measured with a Chlorine Meter Scale, using a wavelength of 530 nm. The readout is given directly in ppm chlorine.

High concentrations of chlorine in a sample, in excess of 2 ppm, can cause indicator or meter reading problems, and such samples will require dilution.

Samples with too high acidity or alkalinity may require adjustment to a pH range of 6 to 7 using additions of acid or alkali substances free from chloride or ammonium ions.

Standard test solutions were prepared using sodium chlorate and sodium hypochlorite. The results of the tests carried out are shown in Table 2-7.

It will be noted that the test results show excellent agreement with the standards.

Conclusions

1. The HACH method for the determination of chlorine (total) gives excellent results. Due attention must be paid to situations involving high sample concentrations of chlorine, or high acidity/alkalinity conditions.
2. Adequate stocks of all expendable reagents and solutions should be maintained at home-base.

2.2.2.7 Sodium chromate in cooling waters

This method reports chromate in cooling waters (or

TABLE 2-7

TOTAL CHLORINE DETERMINATION - DR-EL/4 MANUAL, PAGES 2-16 AND 2-17

Chlorine salt	Standard strength (ppm chlorine)	Test value (ppm chlorine)
Sodium hypochlorite, NaOCl	2	2.00
	1	0.90
	0.5	0.45
Sodium chlorate, $NaClO_3$	2	1.92
	1	1.02
	0.5	0.55

Available range: 0 - 2 ppm total chlorine

other waters) as sodium chromate. Sodium chromate is added to cooling waters to inhibit rust formation. The technique of analysis, covered in the DR-EL/4 Manual on pages 2-18 and 2-19, involves a photometric method capable of measuring at 460 nm the yellow colour intensity due to the chromate ion.

Several precautionary measures may be required in actual practice. Turbid samples will require filtration. The sample solution must be alkaline before measurement photometrically, since the chromate ion converts to the orange dichromate form in acid solution. The setting of the examining wavelength at 460 nm must be checked for maximum response using a blank and a standard chromate ion solution.

Tests were made using a standard sodium dichromate solution adjusted to an alkaline zone pH. The results are shown in Table 2-8, and these show good agreement with the standard.

Conclusions

1. The chromate test method outlined in DR-EL/4 provides satisfactory results where the proper precautions have been taken.
2. Adequate supplies of all expendable reagents and solutions must be available on-site and in home-base storage.

2.2.2.8 Copper in waters

The method outlined in DR-EL/4, pages 2-26 to 2-28, is intended to determine the amount of copper in water and waste

TABLE 2-8

CHROMATE DETERMINATION - DR-EL/4 MANUAL, PAGES 2-18 AND 2-19

Reagent	Standard strength (ppm Na_2CrO_4 equiv.)	Test value (ppm Na_2CrO_4 equiv)
Sodium dichromate, $Na_2Cr_2O_7$	999.6	1001

Available range: 0 - 1000 ppm chromate as sodium chromate

water samples. The methodology involves the photometric measurement, at 560 nm wavelength, of the intensity of a purple colour developed in the presence of copper by bicinchononate.

Again, several precautionary steps may be required. These are too lengthy to include here, but are well delineated in the Manual. The final value is obtained from the photometer in ppm copper through the use of a special Copper Bicinchononate Scale.

A test was carried out using a standard solution of copper sulphate. The result is shown in Table 2-9. The technique showed good agreement with the prepared standard.

Conclusions

1. When all precautionary steps have been observed, where these are necessary, the HACH method gives good results in the determination of copper.
2. Many expendable reagents and solutions may be required, particularly where precautionary pre-measurement steps must be taken. These expendables must all be maintained adequately at home-base.

2.2.2.9 Fluoride in waters

The content of fluoride in waters and waste waters is determined by the method outlined in the HACH DR-EL/4 Manual, pages 2-29 and 2-30. The technique involves a photometric determination based on the colour developed by fluoride ion

TABLE 2-9

COPPER DETERMINATION - DR-EL/4 MANUAL, PAGES 2-26 TO 2-28

Copper salt	Standard strength (ppm Cu equiv)	Test value (ppm Cu equiv)
Copper sulphate, $CuSO_4 \cdot 5H_2O$	3.0	3.0

Available range: 0 - 3 ppm copper

in the presence of SPADNS, a dark red zirconium-lake dye. The reaction of fluoride with zirconium forms a colourless complex, diluting the intensity of the dye colour. The diminution in intensity is measured at 580 nm, and the meter scale used provides the result in ppm fluoride directly.

Precautionary measures that may be required are well outlined in the Manual, and do not require repetition here. A test solution was prepared using hydrofluoric acid. The results obtained are shown in Table 2-10.

The value obtained agreed well with the prepared standard value.

Conclusions

1. The HACH method gives good results, providing any necessary precautionary steps are followed exactly.
2. Expendable reagents and solutions must be maintained in adequate quantities in home-base stores.
3. A pipetting bulb must be used when pipetting the SPADNS reagent.

2.2.2.10 Total iron in waters

Total iron in ground and domestic waters is determined by the technique outlined in DR-EL/4, pages 2-35 and 2-36. The method involves the simultaneous reduction of all iron and the development of the orange colour given by the reaction of ferrous iron and 1,10 phenanthroline through the addition of

TABLE 2-10

FLUORIDE DETERMINATION - DR-EL/4 MANUAL, PAGES 2-29 AND 2-30

Fluoride salt	Standard strength (ppm F equiv)	Test value (ppm F equiv)
Hydrofluoric acid, HF	2.00	1.95

Available range: 0 - 2 ppm fluoride

a FerroVer Iron Reagent. A photometric reading is made at 510 nm, and the total iron value in ppm is expressed directly from the special meter scale used.

A variety of precautionary steps may be required, depending on sample solution conditions. Again, these are well outlined in the Manual and do not require to be repeated here.

A pair of standard solutions were prepared using ferric chloride. These were tested for total iron content, and the results are shown in Table 2-11.

Agreement with the standard values was good, with some tendency to be slightly high.

Conclusions

1. The method yields satisfactory results for total iron. The indicated tendency to be somewhat high may be confined to this set of tests. In any case, the discrepancy is not of a serious nature. The indicated precautionary steps would have to be applied where solution circumstances so dictate.
2. While it would be important to maintain adequate stocks of all expendable reagents and solutions at home-base stores, it should be noted that the FerroVer Iron Reagent Powder has a shelf-life which can change for the worse if stored in a warm, wet atmosphere. This should be given consideration when arranging for adequate stocks of this reagent.

TABLE 2-11

TOTAL IRON DETERMINATION - DR-EL/4 MANUAL, PAGES 2-35 AND 2-36

Iron salt	Standard strength (ppm Fe equiv)	Test value (ppm Fe equiv)
Ferric chloride, $FeCl_3$	1.0	1.1
	2.0	2.2

Available range: 0 - 2 ppm total iron

2.2.2.11 Nitrogen, ammonia in waters

This technique is intended to determine the quantity of nitrogen as ammonia in water and waste water samples. In natural surface waters the presence of ammonia usually indicates domestic pollution; its presence in ground waters is normal. The method is given in DR-EL/4, pages 2-39 to 2-40. The technique involved is the Nessler method, where ammonia reacts with the Nessler reagent to yield a yellow colour the intensity of which is a measure of the amount of ammonia present in the sample. The method of examination is photometric, using a wavelength of 425 nm and a Nitrogen Ammonia Meter Scale which gives the nitrogen, ammonia in ppm.

High hardness water samples may require treatment with Rochelle Salt Reagent to avoid interference by the precipitation of magnesium hydroxide. Interferences results from the presence of iron and sulphide, as well as from that of various organic compounds. The presence of these interfering substances may require that the sample is distilled.

Standard concentration solutions were prepared from a number of ammonium ion compounds. These were subjected to the test procedure and gave the results shown in Table 2-12.

Although two out of three results were on the low side, the test can be considered to have given reasonable valid results.

Conclusions

1. The DR-EL/4 Manual technique provides somewhat low but satisfactory results in the determination of ammonia

TABLE 2-12

NITROGEN, AMMONIA DETERMINATION - DR-EL/4 MANUAL, PAGES 2-39 AND 2-40

Nitrogen ammonia salt	Standard strength (ppm NH_3 equiv)	Test value (ppm NH_3 equiv)
Ammonium acetate, $CH_3 \cdot COONH_4$	2.0	1.6
Ammonium chloride, NH_4Cl	2.0	2.0
Ammonium sulphate, $(NH_4)_2SO_4$	2.0	1.8

Available range: 0 - 2 ppm NH_3 nitrogen

nitrogen in water samples.

2. There are several possible interfering solution conditions, and these have to be dealt with in accordance with the instructions in the Manual.

3. Adequate stocks of expendable reagents and solutions must be maintained in home-base stores. In arranging for an appropriate stock, it must be remembered that the Nessler Reagent has a shelf life of about one year.

4. The Nessler Reagent may, quite normally, develop a precipitate at the bottom of its container. When obtaining solution from the bottle it is important to avoid disturbing these solids. Incorporation of solids in the Nessler Reagent withdrawn for test purposes can lead to erratic results.

2.2.2.12 Nitrogen, nitrate in waters

This technique, outlined in HACH DR-EL/4 pages 2-41 and 2-42, is intended to determine the amount of nitrogen present as nitrate in water and waste water samples. The method is a modification of the cadmium reduction technique, with gentisic acid being used in place of 1-naphthylamine. The reaction develops a brown colour if nitrate nitrogen is present. The intensity of the colour is dictated by the amount of nitrate present, and is determined photometrically at 500 nm. Use of a specific nitrate nitrogen meter scale permits the result to be expressed directly as ppm of nitrate nitrogen.

There are strict instructions regarding colour development, as well as for the elimination of interfering conditions. These are well outlined in the Manual, and do not require repetition here.

Several nitrate compounds were used to prepare standard solutions of nitrate nitrogen. These were submitted to the test conditions. The results obtained are shown in Table 2-13. While these results are good in some instances, they were less so in others.

Conclusions

1. It was felt by the investigators that the instructions for the development of the brown colour due to nitrate leaves a lot to be desired with respect to both time of shaking and time for colour development. The stipulated shaking time of exactly one minute never seemed to be adequate, and at least two minutes appeared to be preferable.

2. Within restrictions relative to possible modification of the shaking and colour development times, the method appeared to yield reasonably satisfactory results.

3. A rather strange situation developed relative to the testing of any standard prepared using ammonium nitrate. The nitrogen, ammonia test had given erratic and high results relative to the ammonium content. With the nitrogen, nitrate test, low results were obtained.

4. The NitraVer colour-developing reagent is temperature sensitive with respect to its reaction, and this is best

TABLE 2-13

NITROGEN, NITRATE DETERMINATION - DR-EL/4 MANUAL, PAGES 2-41 AND 2-42

Nitrate salt	Standard strength (ppm NO_3 equiv)	Test value (ppm NO_3 equiv)
Potassium nitrate, KNO_3	30	30
Sodium nitrate, $NaNO_3$	30	31
Ammonium nitrate, NH_4NO_3	30	21
Nitric acid, HNO_3	30	25

Available range: 0 - 30 ppm NO_3 nitrogen

carried out between 20° and 24°C. It is apparent that a heating process may frequently be required.

5. Adequate stocks of all expendable reagents and solutions must be maintained in home-base stores.

2.2.2.13 Phosphorus in waters

The HACH DR-EL/4 Manual describes three separate methods for the determination of phosphorus in waters. Pages 2-52 and 2-53 describe a technique for the determination of phosphorus when present as orthophosphate. Pages 2-54 and 2-55 outline the technique to be used when the phosphorus is present in the pyro-, meta- or poly-phosphate forms. On pages 2-56 and 2-57, a technique is described for the determination of phosphorus when present in the organically-bound form.

The first technique involves the determination of phosphorus by a modification of the molybdenum blue method. This is a photometric technique, with examination at 700 nm. The appropriate meter scale allows the direct reading of phosphate in ppm.

The subsequent two techniques use preparatory procedures distinct for each, but the final determination stage is identical to that for the first technique.

In order to avoid carrying out separate determinations for each method, the investigators classed the techniques as Methods 1, 2 and 3 in the order given above. Various standards were prepared involving ortho-, poly- and organic-phosphate

compounds. Each standard was subjected to all methodologies. Table 2-14 indicates the results obtained. The proper methodology to be applied is asterisked, and it is the result for this methodology that is the most significant.

In general, the results of all tests were quite satisfactory.

Conclusions

1. Within the limitations of the testing program, the HACH DR-EL/4 techniques appear to provide satisfactory methods for the determination of the three forms of phosphate. The importance of generally adhering to the proper methodology is apparent.
2. Interferences are listed in the methodologies, and the methods for eliminating these interferences, where possible, are well-outlined in the Manual.
3. Extension of the normal range to a low-range capability of 0 to 0.15 ppm is possible with accessory equipment.
4. Adequate stocks of all expendable reagents and solutions should be maintained at home-base stores at all times.

2.2.2.14 Silica in waters

This test is intended to determine the amount of silica present in water samples, and the technique is outlined in the DR-EL/4 Manual, pages 2-60 and 2-61. The methodology involves ammonium molybdate/phosphate photometric technique. The blue

TABLE 2-14

DETERMINATION OF PHOSPHORUS, REACTIVE, ACID HYDROLYZABLE AND ORGANIC - DR-EL/4 MANUAL, PAGES 2-52 TO 2-57 INCLUSIVE

Phosphate salts	Standard strength (ppm PO_4 equiv)	Test value (ppm PO_4 equiv)	
Potassium hydrogen phosphate, K_2HPO_4	2	*Method 1	2.0
		Method 2	2.4 approx
		Method 3	0.6
Sodium dihydrogen phosphate, NaH_2PO_4	2	*Method 1	2.1
		Method 2	2.1
		Method 3	0.2
Sodium pyrophosphate, $Na_4P_2O_7$	2	Method 1	0.1
		*Method 2	1.7
		Method 3	2.2
Calcium dihydrogen phosphate, $Ca(H_2PI_4)_2$	2	*Method 1	2.0
		Method 2	1.6
		Method 3	1.6
Calcium monohydrogen phosphate, $CaHPO_4$	2	*Method 1	1.8
		Method 2	2.0
		Method 3	1.8
Phosphoric acid, H_3PO_4	1.7	*Method 1	1.6
		Method 2	1.6
		Method 3	1.4
Malathion, organophosphate pesticide	about 2	Method 1	0.6
		*Method 2	1.5
		Method 3	1.8

Available range: 0 - 2 ppm PO_4

colour development is measured as to intensity photometrically at 700 nm, and the use of the appropriate meter scale attachment permits the reading of silica directly in ppm.

A standard concentration sample was prepared using sodium metasilicate. Because of a degree of uncertainty in knowing the exact composition of this compound, the preparation could only be approximate as to strength. The result obtained is shown in Table 2-15 and, within the limitations involved, would appear to be satisfactory.

Conclusions

1. The test method appears to yield satisfactory results in the determination of silica.
2. Interferences can be minimized or eliminated by following the procedures outlined in the Manual.
3. Possible presence of silica in demineralized water under certain conditions demands that the demineralized water be subjected to the normal silica test as a background determination.
4. Expendable reagents and solutions should be maintained in adequate quantities in home-base stores.

2.2.2.15 Sulphate in waters

The techniques for the determination of sulphate in waters and waste waters is outlined in the DR-EL/4 Manual, pages 2-62 and 2-63. The method is based on determining the

TABLE 2-15

SILICA DETERMINATION - DR-EL/4 MANUAL, PAGES 2-60 AND 2-61

Silica salt	Standard strength (ppm SiO_2 equiv)	Test value (ppm SiO_2 equiv)
Sodium metasilicate, $Na_2SiO_3 \cdot 9H_2O$	about 2	2.45

Available range: 0 - 2 ppm SiO_2

sulphate by measuring the turbidity resulting from the precipitation of barium sulphate. This is done photometrically at a wavelength of 450 nm.

In order to ensure a reasonable proximity to a standard particle size for the barium sulphate, instructions concerning the precipitation process must be followed rigidly.

Various sulphate salts were used to prepare standard solutions for test purposes. The results of the tests are shown in Table 2-16. In the main these appear to be quite satisfactory.

2.2.3 HACH DR-EL/4 investigations remaining

Several of the HACH DR-EL/4 Manual tests remain to be carried out under experimental conditions. These will be completed before September, 1982. Subsequent reports covering the Contract extending the program into 1982-83 will cover the completion of these tests and the reporting of the results.

2.2.4 General conclusions relative to the HACH DR-EL/4 kit tests

2.2.4.1 Limitations as to the media of application

It should be remembered that these tests were devised basically for the examination of samples of natural waters, domestic waters and, with exceptions as to origin, waste waters. They will not be applicable to badly-contaminated waters originating with fouled rivers or streams, industrial and commercial processes, etc. They may not even be applicable

TABLE 2-16

SULPHATE DETERMINATION - DR-EL/4 MANUAL, PAGES 2-62 AND 2-63

Sulphate salts	Standard strengths (ppm SO_4 equiv)	Test values (ppm SO_4 equiv)
Magnesium sulphate, $MgSO_4$	150	160
Zinc sulphate, $ZnSO_4$	150	175
Ammonium sulphate, $(NH_4)_2SO_4$	150	150
Copper sulphate, $CuSO_4$	150	150
Sodium sulphate, Na_2SO_4	150	140
Sulphuric acid, H_2SO_4	150	135
Aluminum sulphate, $Al_2(SO_4)_3$	150	160
Potassium sulphate, K_2SO_4	150	150

Available range: 0 - 150 ppm SO_4

to water samples taken at spill sites where the water is badly contaminated with respect to high concentrations of the analytes involved or with respect to critical concentrations of substances capable of interfering with the methodology involved.

It may be very well to consider that samples of waters bearing high concentrations of the analytes of interest can be treated by a process of dilution, but it must be remembered that with excessive dilution, and the associated multiplying factors, comes increasingly poor precision and accuracy.

2.2.4.2 Limitations as to application

Most of the techniques outlined in the DR-EL/4 Manual are titrimetric with colour-change indicator endpoint location, or photometric based on colour intensity/concentration relationships. It is at once apparent that these techniques will suffer where attempts are made to apply them to samples that are turbid or highly-coloured. While turbidity can often be removed by a filtration process, this procedure is not always successful with suspended or colloidal organic or inorganic suspensions. Highly-coloured samples will, of course, mask the indicator colour changes or the photometric colour-development.

Another factor of importance is the effect of certain types of solution contaminants such as high molecular weight substances of an organic nature (e.g. proteins, gels, etc.) on the colour-change reaction of certain indicator types,

particularly the acid-base indicators used in acid/base titrations.

It should always be remembered that the reactions involved in the tests carried out according to the DR-EL/4 Manual will be temperature sensitive. It cannot be expected that these reactions will go sufficiently if attempts are made to carry them out at the level of ambient temperatures found outdoors in Canadian winters. The need for site van laboratories that are heated to reasonable temperatures is obvious.

2.2.4.3 Limitations as to methodologies

Nearly all of the DR-EL/4 methods provide for a checking technique involving the use of the standard additions method. Such checking techniques will nearly always be successful where it is felt necessary for them to be applied to those methods that are photometric. They are less likely to work well when applied to the titrimetric methods since, in most instances, the high-strength titrant used requires drop-splitting and extreme care in carrying out the methodology in order to come anywhere near the expected standard addition/titrant volume increase expected.

2.2.4.4 General applicability

All of the methods outlined for the HACH DR-EL/4 kit, and tested so far in this investigation, showed reasonable

accuracy within the restrictions and limitations outlined in the foregoing.

2.3 OVA/PTD Investigations - Level II Methods

2.3.1 General

The project delays resulting from operational, repair and delivery problems arising out of the OVA/PTD equipment have already been outlined in Section 1 and in Appendix B. These delays resulted in the program being incomplete within the time span of the 1981-82 Contract. Nevertheless, a very considerable amount of exploratory work was carried out, and the methodologies of standard vapour sample preparation and instrument calibration were well established.

Although the OVA/PTD instrument manuals suggested the one-time use of green garbage bags as a means of preparing standards and test samples of organic vapours, it was found that this type of container yielded reaction or absorbance situations with certain organic substances, leading to erroneous and erratic results. This was eventually corrected through the use of aluminized polyester (Mylar) sampling bags, although the late delivery of these bags prevented completion of the program by March 31, 1982. The same general methodologies developed using the garbage bags are being presently applied with the new collecting bags successfully.

This Report covers the details of the work of investigation

carried out for the 1981-82 Contract. It should be realized, however, that much of this work has been and is being repeated using the more suitable polyester collecting bags.

2.3.2 Calibration of the OVA in the "Sniffer" mode

There is no need to provide here the complete details with respect to the technique used in the calibration of the OVA in the "sniffer" mode, since these will be included in the OVA/PTD Operational and Training Manual now well on its way to completion.

The calibration procedure is carried out against methane gas. Since each responding organic vapour provides for a different response from the flame ionization detector (FID) of the OVA, it is essential that the instrument be calibrated for each FID-sensitive substance. These various calibrations are then each reported as "response relative to methane". In all of the tests applied, therefore, the reports involved carry, for each organic substance, the datum "Relative Response:", followed by the response as a percentage of the response for methane.

2.3.3 Preparation and use of vapour standards

2.3.3.1 Preparation of vapour standards

Again, detailed information on the preparation procedures need not be supplied here, since the Operational and Training Manual for the OVA/PTD will provide such details. It will be

sufficient to indicate, in this section of the Report, that the samples were prepared by injection into green garbage bags (now polyester bags) the volume of organic liquid required to yield a particular standard concentration. The zero of background level was measured on a standard involving air only.

2.3.3.2 Testing of vapour standards, "sniffer" mode - bag problems

Each of the prepared standard samples in a series was tested. In each series of tests, two sets of readings were obtained; one when the mixture had equilibrated (about 5 minutes generally) and the other 30 minutes later. The test possibilities were:

(1) Where the second set of readings is higher than the first by more than the experimental error factor, it can be assumed either that the organic substance has attacked the bag material and released another FID-sensitive substance or that the gas mixture had not had sufficient time to equilibrate properly at the time of the first test.

The latter situation is easily investigated by an extension of the equilibration time, and this will either confirm or displace the assumption. The former situation, which occurs with certain substances and with the use of the green garbage

bags, was usually found to be at the root of the problem.

(2) Where the second set of readings is lower than the first by more than the experimental error factor, it can be assumed that either the organic vapour has been absorbed by the bag material or, again, that equilibration was incomplete at the time of the first test.

Again, with the latter situation eliminated or confirmation can be achieved by testing at extended equilibration times. The former situation, which occurs with green garbage bags and certain types of organic substances, was normally found to lie at the root of the problem.

(3) The second set of readings agrees with the first within the factor of experimental error. Equilibration time here has been adequate and neither FID-sensitive release nor absorbance actions have taken place.

Normally, at least two series of tests were made, each series using once-only garbage bags for each sample.

Figure 2-1 shows an example of a situation where the action of the organic vapour has released from the garbage bag material an FID-sensitive substance. The organic vapour involved is acetone, and the three trial plot sets are shown.

The solid line in all plots represents the first tests run after the equilibration time, while the dashed line represents the test runs carried out 10 minutes after the first test runs. The elevation of the readings for the second tests is obvious in each case.

Figure 2-2 shows an example of the situation where the organic vapour has been absorbed to a degree by the garbage bag material. The substance involved is benzene, and the three trial plots are shown. Again, the solid line represents the first test and the dashed line the second test, and it will be noted that the second set of tests shows a plot line much lower than that for the first set in all three trials.

Figures 2-3 and 2-4, representing respectively one each of the trial plots for toluene and o-xylene, show the same situation to even greater degrees. The other two sets of plots for each substance showed exactly the same degree of difference in each case.

These problems will, of course, be corrected by the use of aluminized polyester bags.

Figure 2-5 shows a situation where the three plots show between the first and second sets of test readings that are attributable only to experimental error. The vapour substance involved in these instances was acetic acid.

Table 2-17 gives a summary of the test results obtained with respect to problems with the green garbage bags.

FIGURE 2-1

THREE PLOTS FOR CALIBRATION OF ACETONE
VAPOUR STANDARDS - GREEN GARBAGE BAG COLLECTION

OVA unit - "sniffer" mode

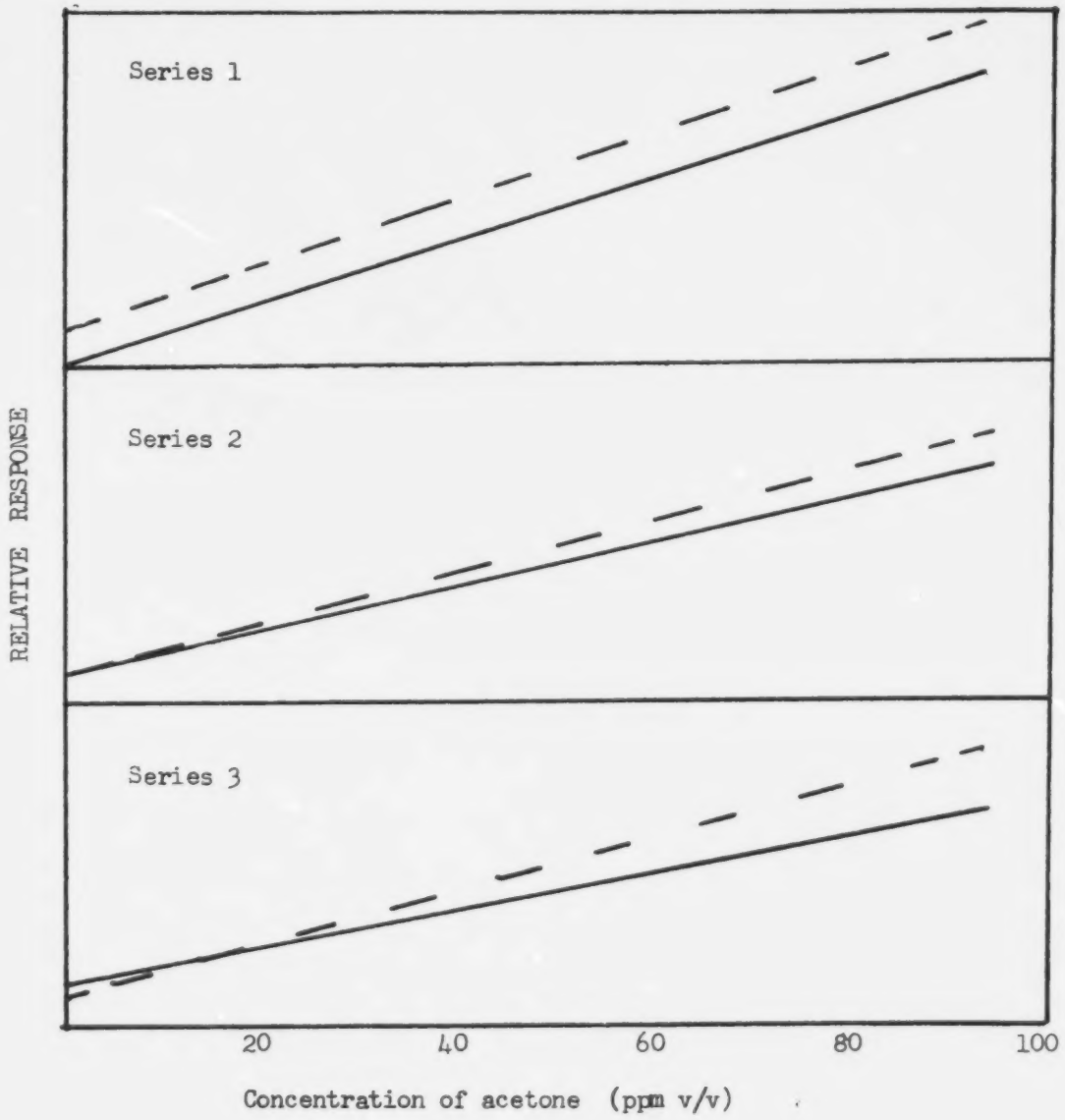


FIGURE 2-2

THREE PLOTS FOR CALIBRATION OF BENZENE
VAPOUR STANDARDS - GREEN GARBAGE BAG COLLECTION

OVA unit - "sniffer" mode

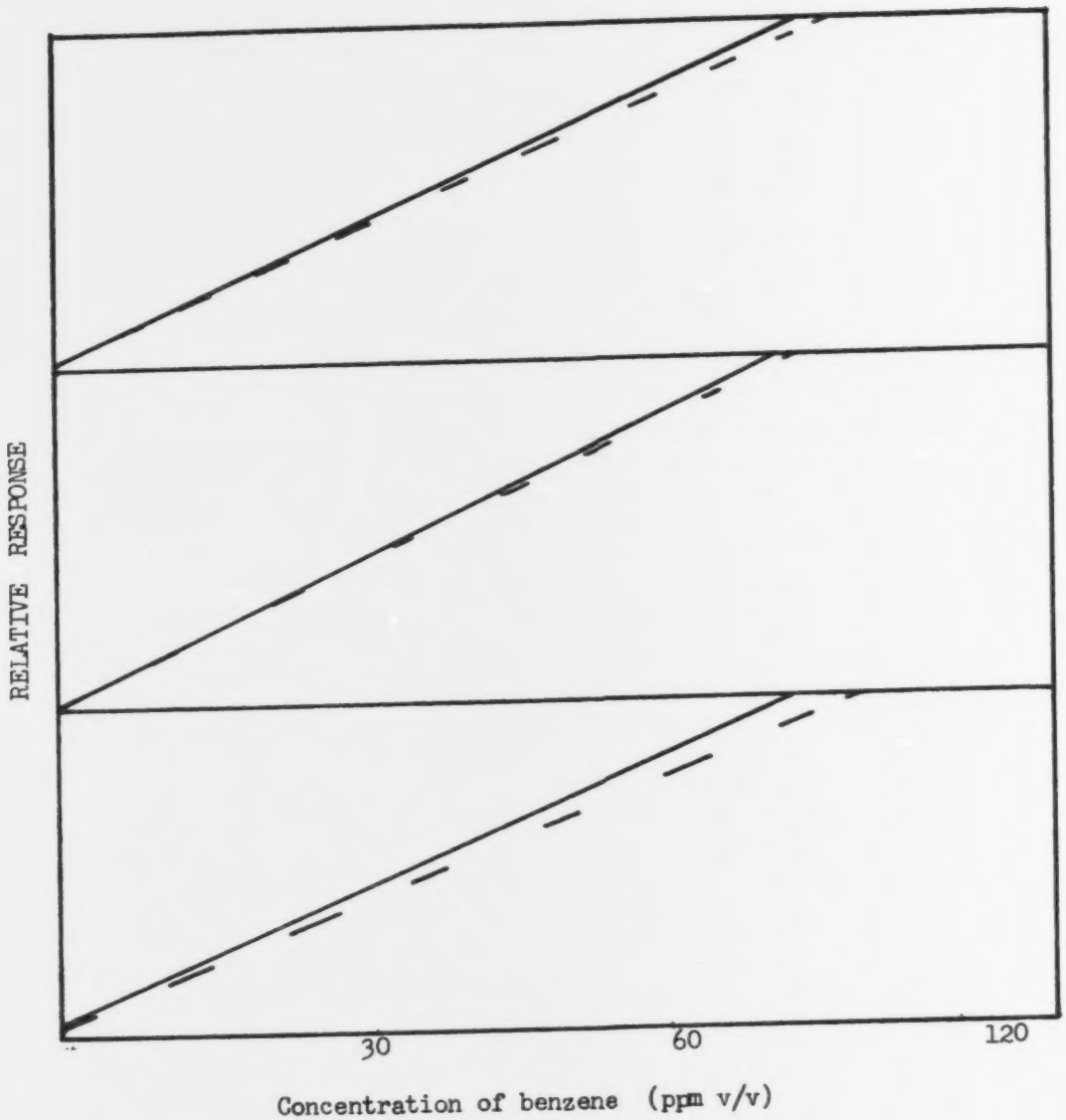


FIGURE 2-3

PLOT FOR CALIBRATION OF TOLUENE VAPOUR STANDARDS - GREEN GARBAGE BAG USAGE

OVA unit - "sniffer" mode

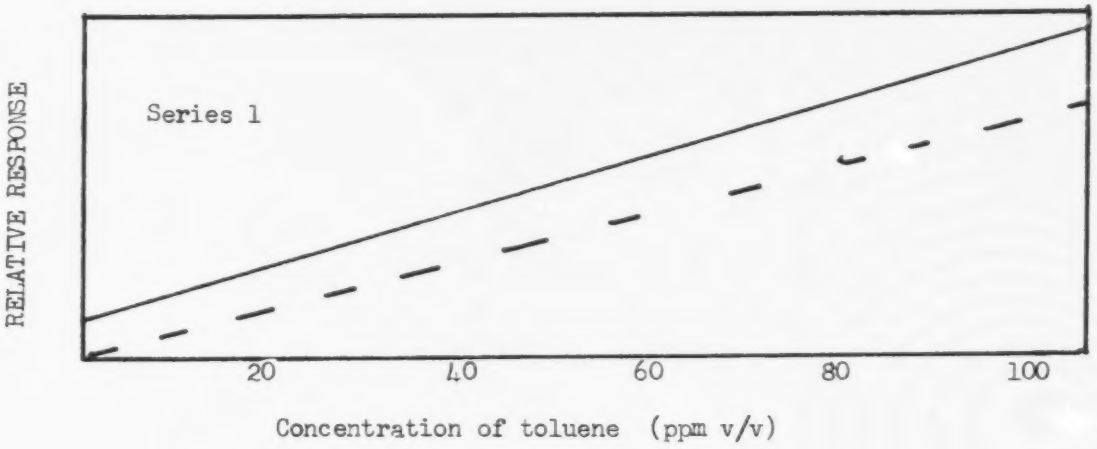


FIGURE 2-4

PLOT FOR CALIBRATION OF O-XYLENE VAPOUR STANDARDS - GREEN GARBAGE BAG USAGE

OVA unit - "sniffer" mode

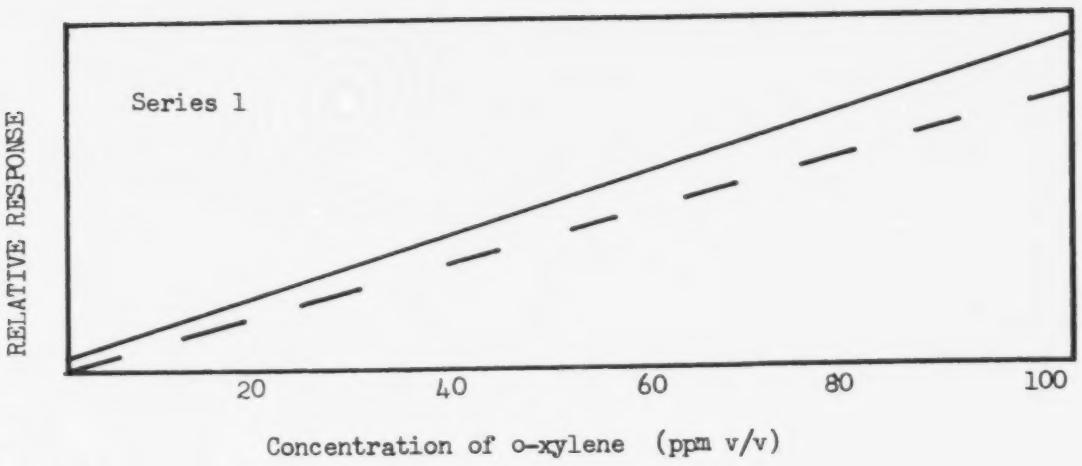


FIGURE 2-5

THREE PLOTS FOR CALIBRATION OF ACETIC ACID VAPOUR STANDARDS - GREEN GARBAGE BAG COLLECTION

OVA unit - "sniffer" mode

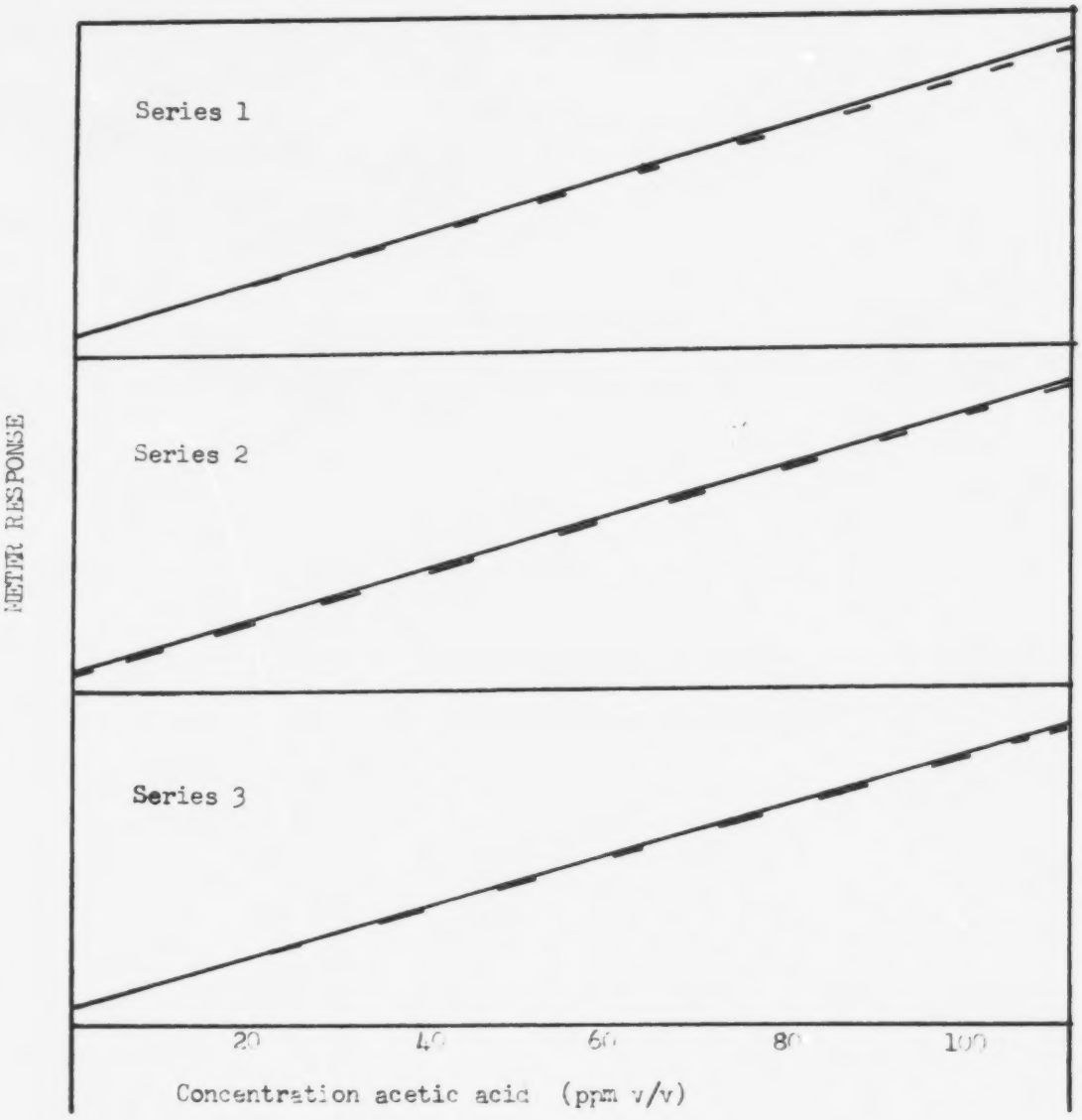


TABLE 2-17

GREEN GARBAGE BAG TESTS ON VAPOUR STANDARDS - OVA "SNIFFER" MODE

First test results higher than second	First test results lower than second	Both test results same within experimental error
benzene	acetone	acetic acid
cumene		acetic anhydride
ethyl benzene		butanol
ethylene dichloride		cyclohexane
2-methoxy ethanol		n-hexane
morpholine		methanol
toluene		methyl isobutyl ketone
o-xylene		methylene chloride

Note: First test readings taken after equilibration period; second test readings taken 10 minutes after the first readings.

2.3.3.3 OVA testing of vapour standards in "sniffer" mode - test results

Appendix C lists the test results for two of three series of tests on various organic compound vapour standards. The compounds involved are from the lists of priority hazardous substances. Each series involved different once-only use garbage bags for each sample in the series, and each sample was tested at equilibration and 30 minutes later.

The data in Appendix C provides the relative response factor for the compound involved, the coefficient of correlation (r) for the regressed data, the y- or relative response axis intercept for the line and the line slope. Serious differences in the y-intercept and/or slope for each test series, with respect to the equilibration and 10 minute delay readings, can indicate problems absorbance by the garbage bag material or release from this material of FID-sensitive substance(s). It should be remembered, however, that the results being obtained now, and to be obtained, with the new polyester bags will differ from those in Appendix C only where such absorbance or release mechanism existed. It will be noted, generally, that all of the test series results listed in Appendix C show good values of the coefficient of correlation, indicating good linear response situations. It will be noted also that, in general, the degree of release of FID-sensitive material or the degree of absorbance increases proportionately with the increasing concentration of active organic vapour present.

2.3.3.4 Conclusions

Apart from the problems encountered with respect to the use of green garbage bags for standard sample preparation work, the tests carried out so far indicate that the OVA/PTD equipment works extremely well in the "sniffer" mode.

2.3.3.5 Work in progress

"Sniffer" mode tests have been completed since the March 31, 1982 closing date of the 1981-82 Contract. Tests of the OVA/PTD in the survey or GC mode are well underway and should be completed by January, 1983 at the latest. Only aluminized polyester (Mylar) collecting bags are now being used.

2.4 HNU/PI Investigations - Level II Methods

As indicated in Section 1, equipment delivery delays and operational problems held up any worthwhile exploratory work with respect to the HNU photoionization detector during the period of the 1981-82 Contract. Some calibration work was carried out prior to the March 31, 1982 deadline but, since this involved the use of green garbage bags, the results can only be considered to be dubious.

Work is now well underway in connection with all tests involving the HNU, and will be completed around the end of 1982. Indications are, at the moment, that the HNU performs satisfactorily for those hazardous substances tested so far that have sensitivity to the eV value for the photoionization detector.

3. UV-VIS/IR COMPUTER LINKED INVESTIGATIONS - LEVEL III METHODS

Initially a method to record standard, known spectra for qualitative analysis was adapted for use in both qualitative and quantitative analysis in the field.

It was considered highly desirable to use the minimum of data points to adequately record spectra for subsequent qualitative identification and quantitative analysis of mixtures of different compounds. From previous experience it was concluded that 120 data points per spectra yields sufficient qualitative resolution and 0.0 to 1.0 absorbance sufficient quantitative resolution.

Initially spectra were entered manually by recording the 120 data points in the Data Format to Enter/Edit Data Page, Appendix D.

It was soon considered desirable to automate the data acquisition for samples and standard spectra. This required the development of the Data Acquisition System, Appendix E.

It was then desired to acquire data from the instruments in the system which have analog data outputs in the range of 0 to +5 V. This required generalizing the Data Format to Enter/Edit Data, Appendix F. Since the output voltages of the different instruments vary substantially in output voltage ranges it is necessary to have a variable gain amplifier at each instrument output to adjust its range from 0 to +x V to to 0 - x V to obtain data points between 0 and 999 to obtain two significant figures.

Finally a Computer Interface Module, Appendix G, of eight ports selected and controlled by the computer to collect data from one analytical system at a time. The parameters of the instrument are set and entered in the computer as in Appendix D.

The computer programs were developed by Mr. F. Tomas and the interface module was designed by Mr. J. Blaison of Concordia University. They will be available for any modifications that may be required in the near future, after delivery of the system.

The computer interface module is a system to control the transfer of data from any one of eight sources of analog data or any one, of four, sources of digital data. In addition it is equipped with four digital outputs.

Each analog input can respond to voltages in the range of 0 to +5 volts DC with a resolution of 8 bits (1 in 256) with an input impedance of 10 megohms and are protected against accidental overloads.

The computer interface module is simple and economically easy to use and can be connected to any computer equipped with a standard RS232 entry port.

The four digital inputs are protected by high impedence inputs and can be directly connected to TTL or CMOS circuits. In addition to communication with standard RS232 entry ports it is possible to communicate by means of telephone lines or by radio and a modem unit.

The block diagram indicating the different steps in

the operation of the computer interface module is shown in Appendix G.

3.1 Computer Analyst Aids

The set of analyst aids, listed below, were developed to calculate absorbances at specified concentrations, molar absorptivities, absorbances in parts per millions, vapor pressure by liquid evaporation and at specified temperatures.

Aid #1 - Absorbance of a liquid at concentration (c)

Aid #2 Absorbance of a solid at concentration (c)

Aid #3 - Absorbance of a vapor at concentration (c)

Aid #4 - Vapor pressure determination at specified temperatures

Aid #5 - Vapor pressure by liquid evaporation in gas cell

Aid #6 - Molar absorptivity of a liquid

Aid #7 - Molar absorptivity of a solid

Aid #8 - Molar absorptivity of a vapor

Aid #9 - Absorbance of a gas parts per million - ppm

Aid #10 - Absorbance of a liquid in parts per million - ppm

Aid #11 - Absorbance of a solution in parts per million - ppm

Aid #12 - Absorbance of an aerosol in parts per million - ppm

AID #1 - ABSORBANCE OF A LIQUID AT CONCENTRATION (c)

$$A(c) = \frac{A(m) \times D(l) \times l \times V(l)}{MW \times V(s)}$$

The required data is:

A(m) - Molar absorptivity in absorbance/mole·cm
D(l) - Density of liquid in g/ml
l - Pathlength of cell in cm
MW - Molecular weight in g/mole
V(l) - Volume of liquid in microliter, µl
V(s) - Volume of solution in ml

AID #2 - ABSORBANCE OF A SOLID AT CONCENTRATION (c)

$$A(c) = \frac{A(m) \times l \times w}{MW \times V(s)}$$

The required data is:

A(m) - Molar absorptivity in absorbance/mole·cm
l - Pathlength of cell in cm
MW - Molecular weight in g/mole
V(s) - Volume of solution in ml
w - Weight of solid in mg

AID #3 - ABSORBANCE OF A VAPOR AT CONCENTRATION (c)

$$A(c) = \frac{A(m) \times D(l) \times l \times V(l)}{MW \times V(c)}$$

The required data is:

A(m) - Molar absorptivity in absorbance/mole·cm
D(l) - Density of liquid in g/ml
l - Pathlength of cell in cm
MW - Molecular weight in g/mole
V(c) - Volume of gas cell in ml
V(l) - Volume of liquid in microliter, µl

AID #4 - VAPOR PRESSURE DETERMINATION AT SPECIFIED TEMPERATURES

The vapor pressure of a compound at any specified temperature lower than the boiling point may be determined from the following equation derived from the Clausius-Clapeyron equation.

$$\log p = \log p_{760} - \frac{PHI}{273.16 - t - 0.15\Delta t} \qquad (1)$$

where: PHI - Entropy of vaporization at 760 mm of pressure

t - Boiling point in ^{o}K

Δt - Difference between the normal boiling point, t_h, and the boiling point at reduced pressure, t_1.

If the value of PHI is not readily available but the boiling points at two pressures are available it is possible to calculate the vapor pressure at any specified temperature after calculating the entropy of vaporization from the formula:

$$PHI = \frac{(273.16 - t_1 - 0.15\ (t_h - t_1)\ (\log p_h - \log p_1)}{(t_h - t_1)} \qquad (2)$$

where: p_h is the higher vapor pressure at the higher temperature t_h

p_1 is the lower vapor pressure at the lower temperature t_1

The vapor pressure p_s at any specified temperature t_s is calculated by substituting the value of PHI from equation (2) in equation (1) with equation (3).

$$p_s = 10\left\{\log p_h - \left[\frac{PHI \times (t_h - t_s)}{273.16 - t_s - 0.15(t_h - t_s)}\right]\right\} \qquad (3)$$

The required data is:

t-high - Temperature ^{o}C at high pressure (mm)

t-low - Temperature ^{o}C at low pressure (mm)

t-spec - Temperature ^{o}C as specified in experiment

p-high - Vapor pressure (mm) at high temperature (^{o}C)

p-low - Vapor pressure (mm) at low temperature (^{o}C)

AID #5 - VAPOR PRESSURE BY LIQUID EVAPORATION IN GAS CELL

Vapor spectra of volatile liquids may be recorded at different concentrations in gas cells. The maximum concentration is a function of the vapor pressure of the liquid at the temperature of the experiment, as calculated in Analyst aid #4.

For this purpose the most convenient units are millimeters of Hg for the pressure and milliliters or microliters for the volume of liquid to be evaporated at the specified temperature. Hence the gas constant R is converted as follows.

$$R = 0.08206 \frac{\text{Liter x Atm}}{\text{Mole x } ^{o}\text{K}} \times \frac{1000 \text{ ml}}{\text{Liter}} \times \frac{760 \text{ mmHg}}{\text{Atm}} = 62361 \frac{\text{ml x mmHg}}{\text{mole x } ^{o}\text{K}}$$

It is to be noted that the absorbance in the cell resulting from the evaporation of the liquid is directly related to the molar concentration and the cell pathlength.

If all the experiments are conducted with the same cell, at a fixed pathlength and at constant temperature then the ratio of any two absorbances are directly related to the ratio of the vapor pressures.

The volume of liquid V(1) in milliliters and in microliters is calculated from the equation below.

$$V(1) = \frac{V(c) \times P(v) \times MW}{62361 \times D(1) \times (273.16 - T^{o}C)}$$

The required data is:

D(1) - Density of liquid in g/ml

MW - Molecular weight in g/mole

P(v) - Pressure of liquid vapors in cell in mm-Hg

$T^{o}C$ - Temperature in ^{o}C

V(c) - Volume of cell in ml

AID #6 - MOLAR ABSORPTIVITY OF A LIQUID

$$A(m) = \frac{A(c) \times MW \times V(s)}{D(1) \times 1 \times V(1)}$$

The required data is:

A(c) - Absorbance at concentration (c)

D(1) - Density of liquid in g/ml

1 - Pathlength of cell in cm

MW - Molecular weight in g/mole

V(1) - Volume of liquid in microliters, µl

V(s) - Volume of solution in ml

AID #7 - MOLAR ABSORPTIVITY OF A SOLID

$$A(m) = \frac{A(c) \times MW \times V(s)}{1 \times w}$$

The required data is:

A(c) - Absorbance at concentration (c)

1 - Pathlength of cell in cm

MW - Molecular weight in g/mole

V(s) - Volume of solution in ml

w - Weight of solid in mg

AID #8 - MOLAR ABSORPTIVITY OF A VAPOR

$$A(m) = \frac{A(c) \times MW \times V(c)}{D(1) \times 1 \times V(1)}$$

The required data is:

A(c) - Absorbance at concentration (c)

D(1) - Density of liquid in g/ml

1 - Pathlength of cell in cm

MW - Molecular weight in g/mole

V(c) - Volume of gas cell in ml

V(1) - Volume of liquid in microliters, µl

AID #9 - ABSORBANCE OF A GAS IN AIR IN PART PER MILLION - ppm

$$A(ppm) = \frac{A(ppm)/cm \times V(g) \times 1}{V(air)}$$

The required data is:

A(ppm) - ppm Absorptivity in absorbance/ppm·cm
1 - Pathlength of cell in cm
V(air) - Volume of air in cubic meters
V(g) - Volume of gas in ml

To determine A(ppm)/cm prepare on of the following calibrating mixtures: 50, 250, 1000 ml, etc, of gas in a cubic meter of air; or 50, 250, 1000 microliters, etc, of gas in a liter of air in appropriate pathlength cells.

AID #10 - ABSORBANCE OF A LIQUID IN AIR IN PARTS PER MILLION - ppm

$$A(ppm) = \frac{A(ppm)/cm \times V(1) \times 1}{V(air)}$$

The required data is:

A(ppm) - ppm Absorptivity in absorbance/ppm·cm
1 - Pathlength of cell in cm
V(air) - Volume of air in cubic meters
V(1) - Volume of liquid in ml

To determine A(ppm)/cm prepare one of the following calibrating mixtures: 0.1, 0,5 5.0 ml, etc, of liquid in a cubic meter of air; or 0.1, 0.5, 5.0 microliters, etc, of liquid in a liter of air in appropriate pathlength cells.

AID #11 - ABSORBANCE OF A SOLUTION IN PARTS PER MILLION - ppm

For a liquid:

$$A(ppm) = \frac{A(g) \times D(1) \times V(1) \times 1}{V(sol)}$$

The required data is:

A(g) - Gram absorptivity in absorbance/g·cm
D(1) - Density of liquid in g/ml
1 - Pathlength of cell in cm
V(1) - Volume of liquid in ml
V(sol) - Volume of solution in cubic meter

To determine the gram absortivity in absorbance/g·cm of a liquid dissolve selected volumes from 1.0 to 1000 ml as required per cubic meter of solvent or 1 to 1000 microliters as required per liter of solution.

$$A(g) = \frac{A(ppm) \times V(sol)}{D(1) \times V(1) \times 1}$$

For a solid:

$$A(ppm) = \frac{A(g) \times w(s) \times 1}{V(sol)}$$

The required data is:

A(g) - Gram absorptivity in absorbance/g·cm
1 - Pathlength of cell in cm
V(sol) - Volume of solution in cubic meter
w(s) - Weight of solid in g

To determine the gram absorptivity in absorbance/g·cm of a solid dissolve selected values of 1 to 1000 g as prequired per cubic meter of solvent or 1 to 1000 milligrams as required per liter of solution.

$$A(s) = \frac{A(ppm) \times V(sol)}{w(s) \times 1}$$

AID #12 - ABSORBANCE OF AN AEROSOL IN PARTS PER MILLION - ppm

A specified volume of an aerosol is either directly dissolved or filtered, condensed, trapped and then dissolved in an appropriate solvent to give a specified volume of solution with absorbance A(c). Thus

$$V(\text{aerosol}) \times C(\text{aerosol}) = V(\text{sol}) \times C(\text{sol}) \quad (1)$$

The required data is:

C(aerosol) - Concentration of aerosol in ppm (mg/liter)

C(sol) - Concentration of solution in ppm (mg/liter)

V(aerosol) - Volume of aerosol in liter

V(sol) - Volume of solution in liter

Rearranging equation (1) yields:

$$C(\text{aerosol}) = \frac{V(\text{sol}) \times C(\text{sol})}{V(\text{aerosol})} \quad (2)$$

Since

$$\frac{A(m)}{C(m)} = \frac{A(mg)}{C(mg)} = \frac{C(sol)}{C(sol)}$$

Therefore

$$C(\text{sol}) = \frac{C(mg) \times A(\text{sol})}{A(mg)} \quad (3)$$

Substitution of equation C(sol) from equation (3) in equation (2)

$$C(\text{aerosol}) = \frac{V(\text{sol}) \times C(mg) \times A(\text{sol})}{V(\text{aerosol}) \times A(mg)}$$

The required data is:

A(mg) - Milligram absorptivity in absorbance/mg·cm

A(sol) - Absorbance of solution in absorbance/mg·cm

C(mg) - Concentration in mg/liter, ppm

C(aerosol) - Concentration of aerosol in mg/liter, ppm

V(aerosol) - Volume of aerosol in liter

V(sol) - Volume of solution in liter

3.1.1 Objectives and methods of computer system

The computer system and its programs were designed to interact with the analyst and requires no knowledge of computer programming or computer systems.

Instructions for computer start up only require five simple steps completed in twenty seconds. The analyst is given a program list or menu from which he selects and calls up the desired program, Appendix H.

The computer system notes are simple:

a) any program can be terminated by pressing the "break" key and restarted by pressing "run"

b) to return to the list of the program or menu after pressing the "break" key, press the reset button

The spectroscopy and system allows the development of data bases by entering data manually from previously recorded data with its database program, Appendix I describing the database format, or directly from any instrument that generates a voltage with the dataaqui program, Appendix E.

3.2 Early Investigations and Programs Carried Out

The initial investigation of this part of the Contract involves a computer system and a UV-Visible-IR spectroscopy system for analysis.

3.2.1

The computer system in Section 3.1.1 has been extensively

tested, modified and simplified as the needs of the project and the ease of operation where redefined as the work progressed.

At this point we do not anticipate any substantial modifications of existing methods but rather additions of new analytical techniques are implemented in the future.

The computer system and its programming has been designed to be flexible in terms of additions and minor modifications from experience gained during two years previous to this project.

3.2.2 The UV-Visible-IR spectroscopy system

This system has been investigated to determine its applicability.

The use of UV-Visible spectroscopy is complimentary to other techniques in the presence of aromaticity or chromatographic groups in solutions. A 10-cm pathlength cell is required and preliminary concentration may be required to obtain quantitative results at low concentrations.

For procedures for gases, vapors and by extension to dilute solutions, see Appendices I and J.

The use of IR-spectroscopy is complimentary to other techniques in the presence of strong absorbing functional groups. A 1-meter pathlength cell is required for quantitative analysis with weak absorbing vapors, concentration limits remain to be determined.

For procedures for gases, and vapors, see Appendices K and L.

3.2.2.1 Qualitative IR applications of spectroscopy system

The use of IR spectroscopy is mainly qualitative and semi-quantitative for aromatic compounds and salts. Its main qualitative applications are with liquids and solids.

Computer techniques can substantially enhance the effectiveness of IR spectroscopy to analyze simple mixtures from their patterns. This is illustrated in Appendix M which describes the use of a previously related system used in an analytical organic chemistry laboratory at Concordia University.

3.3 Summary

The Computer System is fully operational for the techniques presently considered. Any required additions should involve only limited modifications of the present system.

The UV-Visible-IR Spectroscopy System is to be developed in conjunction with the other analytical methods to complement them in quantitative analysis of vapors and liquids. It will be one of the main techniques for qualitative analysis of vapors and liquids and the main one for solids.

APPENDIX A

LISTS OF PRIORITY HAZARDOUS MATERIALS FROM THE ENVIRONMENTAL EMERGENCY BRANCH

LIST OF PRIORITY HAZARDOUS MATERIALS FOR THE ENVIRONMENTAL EMERGENCY BRANCH

Group A
The Highest Priority 50 Chemicals
(In Alphabetical Order)

Acetic Acid
Acetic Anhydride
Ammonia
Ammonium Nitrate
Ammonium Phosphates
Benzene
Butyraldehydes
Calcium Chloride
Calcium Oxide/Hydroxide
Carbon Dioxide
Chlorine
Cyclohexane
Ethylbenzene
Ethylene Dichloride (1,2-Dichloroethane)
Ethylene Glycol
Ethylene Oxide
Ethylene
Ferric Chloride
Formaldehyde
Hydrogen Chloride/Acid
Hydrogen Fluoride/Acid
Hydrogen Sulfide
Mercury
Methanol
Morpholine
Naphtha
Natural Gas
Nitric Acid
Phenol
Phosphoric Acid
Phosphorus
Potash (Potassium Chloride)
Propylene Oxide
Propylene
Sodium Chlorate
Sodium Chloride
Sodium Hydroxide
Sodium Hypochlorite
Sodium Sulfate
Styrene (Monomer)
Sulfur Dioxide
Sulfuric Acid (and Oleum)
Sulfur
Tetraethyl Lead
Toluene
Urea
Vinyl Chloride
Xylenes
Zinc Sulfate
2-Ethylhexanol

Group B
The Second Group of Priority Chemicals
(100 substances or groups)

Acetone
Acetylene
Acrylonitrile
Adipic Acid
Aluminum Chloride
Aluminum Hydroxide
Aluminum Sulfate
Aminocarb Pesticide (Matacil)
Ammonium Chloride
Ammonium Sulfate
Arsine

Barium Sulfate
Benzoic Acid
Borax
Boric Acid
Butanols
Butylene
Calcium Carbide
Calcium Carbonate
Calcium Hypochlorite
Calcium Phosphate
Caprolactam
Carbaryl
Carbofuran Pesticides
Carbon Disulfide
Carbon Tetrachloride
Chlordane
Chloroform
Copper Sulfate
Cresols
Dicamba
Dichlorobenzene
Dimethyl Ether
Dimethyl Terephthalate
Dinoseb
Diphenylmethane-4,4'-Diisocyanate

Ethanolamine
Ethanol
Ethylene Dibromide
Fenitrothion
Fluorochloromethanes
Formic Acid
Hydrazine
Hydrogen Peroxide
Hydrogen
Isopropanol
Isopropylbenzene
Latex
Lead Chromate
Lead Oxides

.../

Group B
The Second Group of Priority Chemicals
(100 substances or groups)

Magnesium Hydroxide
Malathion
Maleic Anhydride
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Methyl Metnacrylate
Methylamines
Methylene Chloride
MCPA
n-Hexane
Nitrilotriacetic Acid
Nitroglycerine
Nonyl Phenol
PCBs
Pentachlorophenol
Pentaerythritol
Perchloroethylene
Phthalic Anhydride
Potassium Hydroxide
Potassium Sulfate
Propylene Glycols
Sodium Aluminate
Sodium Arsenite
Sodium Borohydride
Sodium Carbonate
Sodium Cyanide
Sodium Dichloroisocyanurate
Sodium Dichromate
Sodium Hydrosulfite (Dithionite)
Sodium Phosphates
Sodium Silicates
Sodium Sulfite
Sulfuryl Chloride
Tall Oil
Terephthalic Acid
Terphenyls
Titanium Dioxide
Triallate Pesticides
Trichlorfon Pesticides
Trifluralin Pesticides
Trinitrotoluene
Turpentine
Vinyl Acetate
Yellow Cake
Zinc Chloride
Zinc Oxide
1,1,1-Trichloroethane
1,3-Butadiene
2,4-D (2,4-Dichlorophenoxyacetic acid)
2,4-Toluene Diisocyante

APPENDIX B

PROBLEMS ASSOCIATED WITH OVA, HNU AND UV/IR EQUIPMENT

Group B
The Second Group of Priority Chemicals
(100 substances or groups)

Magnesium Hydroxide
Malathion
Maleic Anhydride
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Methyl Methacrylate
Methylamines
Methylene Chloride
MCPA
n-Hexane
Nitrilotriacetic Acid
Nitroglycerine
Nonyl Phenol
PCBs
Pentachlorophenol
Pentaerythritol
Perchloroethylene
Phthalic Anhydride
Potassium Hydroxide
Potassium Sulfate
Propylene Glycols
Sodium Aluminate
Sodium Arsenite
Sodium Borohydride
Sodium Carbonate
Sodium Cyanide
Sodium Dichloroisocyanurate
Sodium Dichromate
Sodium Hydrosulfite (Dithionite)
Sodium Phosphates
Sodium Silicates
Sodium Sulfite
Sulfuryl Chloride
Tall Oil
Terephthalic Acid
Terphenyls
Titanium Dioxide
Triallate Pesticides
Trichlorfon Pesticides
Trifluralin Pesticides
Trinitrotoluene
Turpentine
Vinyl Acetate
Yellow Cake
Zinc Chloride
Zinc Oxide
1,1,1-Trichloroethane
1,3-Butadiene
2,4-D (2,4-Dichlorophenoxyacetic acid)
2,4-Toluene Diisocyante

APPENDIX B

PROBLEMS ASSOCIATED WITH OVA, HNU AND UV/IR EQUIPMENT

OVA/PTD

Generally persistent problems with equipment delivery through Canadian representatives.

(1) July 2, 1981

PTD Unit failed to operate because of SCS-3 solenoid control switch malfunction.

July 23, 1981

New SCS-3 switch replacement received and installed by our own people.

(2) August 12, 1981

PTD pump had been giving intermittent problems. It was felt to be a mechanical rather than an electrical problem, involving perhaps insufficient clearance for the shaft bearing. Finally the OVA unit also failed. The PTD pump, the OVA unit and the probe were sent to Foxboro for repairs on September 29, 1981.

December 7, 1981

The OVA unit was returned without the probe and without the PTD pump. A grid leak was found to exist in the pre-amplication assembly.

April 7, 1982

Still awaiting return of the PTD pump and OVA probe.

(3) Intermittent problems occurred relative to fouling of the chamber for desorbed gas. This had to be cleaned out by several desorb cycles involving Freon 113 gas. It was eventually discovered that Tygon tubing should be avoided, since this material showed pyrolysis with benzene. Only Teflon tubing can be used.

(4) Several repair problems were encountered with respect to the FID unit.

(5) December 4, 1981

New OVA unit delivered could not be calibrated. Eventually located as short in power board.

January 26, 1982

New boards finally arrived at customs. Awaiting papers.

February 15, 1982

New boards finally obtained, installed and equipment operational.

HNU

(1) September 22, 1981

Both units showed poor calibration.

September 23, 1981

Service people carried out re-calibrations. New battery required for one of the units.

November 11, 1981

New battery finally obtained.

(2) March 19, 1982

Two additional HNU units delivered. One was calibrated in error against ethylene oxide.

March 22, 1982

AEL called relative to changing resistor to change calibration to benzene. Supposed to send information.

March 29, 1982

Information received and resistor changed. Equipment still not able to function properly. Resistor changed again, with no better luck.

March 30, 1982

AEL called again, and we were advised that they no longer handle the HNU equipment. Technical Marketing Associates now responsible.

April 2, 1982

Called Technical Marketing Associates - answering service only - left message for representative to call.

April 5, 1982

Representative of TMA called, explained problem to him and was told he would call back.

April 8, 1982

Still awaiting call.

Perkin-Elmer UV Model 552A

(1) November 10, 1981

No keyboard response obtained.

November 13, 1981

P-E service people came in and reported burned-out power boards. Indicated no replacement of these vital parts for 2-3 weeks.

December 1, 1981

Now advised no boards available for an additional 3 weeks. Very strong letter written by Dr. Rye to top P-E administration.

December 13, 1981

New boards received and installed by P-E service people. Problem with keyboard still not resolved.

December 23, 1981

New keyboard installed and unit became functional.

APPENDIX C

LABORATORY TESTS FOR THE OVA "SNIFFER" MODE

CALIBRATION OF ORGANIC VAPOUR STANDARDS

GREEN GARBAGE BAG COLLECTION

ACETIC ACID

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	2.4	2.4
20	2.9	7.8	8.0
40	5.8	10.0	10.0
60	8.7	17.0	17.0
80	11.6	22.0	22.0
100	14.5	28.0	29.0
	r	0.9937	0.9915
	y-intercept	1.8476	1.7333
	Slope	0.2537	0.2600

Relative response: 27% methane

ACETIC ACID

Total sample volume: 62 L

Trial No. 2

ppm	µL	Reading 1st	2nd
0	0	1.0	1.0
20	2.9	6.4	6.2
40	5.8	10.0	9.95
60	8.7	12.0 - ref -	11.5
80	11.6	22.0	21.0
100	14.5	27.0	27.0
	r	0.9981	0.9981
	y-intercept	0.7163	0.6477
	slope	0.2617	0.2580

Relative response: 27% methane

ACETIC ACID

Total sample volume: 62 L

Trial No. 3

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	2.9	5.8	5.7
40	5.8	10.5	10.5
60	8.7	14.0	13.5
80	11.6	17.0	17.5
100	14.5	24.0	23.5
	r	0.9937	0.9964
	y-intercept	1.1857	1.1714
	slope	0.2173	0.2156

Relative response: 23% methane

ACETIC ANHYDRIDE

Total sample volume: 62 L

Trial No.1

ppm	µL	Reading 1st	2nd
0	0	2.8	2.8
20	4.8	9.0	9.0
40	9.6	16.0	16.5
60	14.4	25.0	25.0
80	19.2	33.0	34.0
100	24.0	45.0	45.2
	r	0.9942	0.9984
	y-intercept	0.9429	1.5857
	slope	0.4171	0.3993

Relative response: 42% methane

ACETONE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	3.7	9.6	11.0
40	7.5	16.5	20.0
60	11.2	22.5	30.0
80	15.0	32.0	36.0
100	18.7	46.0	45.0
	r	0.9916	0.9978
	y-intercept	-0.8913	2.0476
	slope	0.4357	0.4357

Relative response: 50% methane

ACETONE

Total sample volume: 62 L

Trial No. 2

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	3.7	9.4	9.2
40	7.5	16.0	16.0
60	11.2	22.0	22.5
80	14.9	31.0	32.0
100	18.7	34.0	35.0
	r	0.9945	0.9948
	y-intercept	2.0571	1.7905
	slope	0.3369	0.3499

Relative response: 36% methane

ACETONE

Total sample volume: 62 L

Trial No. 3

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	3.7	6.7	6.4
40	7.5	12.0	11.5
60	11.2	16.5	17.0
80	15.0	23.0	24.0
100	18.7	27.0	29.0
	r	0.9987	0.9989
	y-intercept	1.2677	0.6524
	slope	0.2620	0.2833

Relative response: 28% methane

BENZENE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	1	1
20	4.5	22.0	23.0
40	9.0	44.0	42.0
60	13.6	79.0	77.0
80	18.1	100.0	99.0
100	22.6	120.0	110.0
	r	0.9968	0.9922
	y-intercept	0.8095	0.9525
	Slope	1.2171	1.1543

Relative response: 120% methane

BENZENE

Total sample volume: 62 L

Trial No. 2

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	4.5	18.0	20.5
40	9.0	41.5	37.0
60	13.6	61.5	60.0
80	18.1	80.5	75.5
100	22.6	100.0	100.0
	r	0.9994	0.9985
	y-intercept	0.2381	0.2143
	slope	1.004	0.9757

Relative response: 99% methane

BENZENE

Total sample volume: 62 L

Trial No. 3

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	4.5	17.5	16.0
40	9.0	36.0	34.0
60	13.6	50.0	47.0
80	18.1	61.0	56.0
100	22.6	83.0	81.5
	r	0.9967	0.9927
	y-intercept	1.8095	1.0000
	slope	1.8095	0.7650

Relative response: 79% methane

BUTANOL

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	3.4	3.4
20	4.7	8.5	8.5
40	10.0	15.0	15.0
60	14.0	21.0	21.0
80	18.6	27.0	28.0
100	23.3	34.0	34.0
	r	0.9986	0.9984
	y-intercept	2.6271	2.5793
	slope	0.3074	0.3116

Relative response: 34% methane

CUMENE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	1	1
20	7.1	10	10
40	14.2	16	15
60	21.2	38 - rej	18
80	28.3	35	27
100	35.4	50	41

r	0.9921	0.9868
y-intercept	-0.3721	1.0233
slope	0.4744	0.3704

Relative response: 47% methane

*NOTE: garbage bag started to dissolve, more evident at higher concentrations.

CYCLOHEXANE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	9	1	1
20	5.5	8.4	9.7
40	11.0	13.0	13.0
60	16.5	22.0	23.0
80	22.0	37.0	38.0
100	27.5	42.0	43.0

r	0.9864	0.9852
y-intercept	-0.8476	-0.4952
slope	0.4283	0.4356

Relative response: 40% methane

CYCLOHEXANE

Total sample volume: 62 L

Trial No. 2

ppm	µL	Reading 1st	2nd
0	0	1.0	1.0
20	5.5	8.6	8.5
40	11.0	14.0	12.0
60	16.5	16.0 - rej.	18.0
80	22.0	24.0	23.5
100	27.5	29.0	30.5

r	0.9967	0.9966
y-intercept	2.2372	1.4048
slope	0.2726	0.2836

Relative response: 30% methane

CYCLOHEXANE

Total sample volume: 62 L

Trial No. 3

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	5.5	7.7	7.4
40	11.0	11.0	10.5
60	16.5	16.0	16.0
80	22.0	21.0	21.0
100	27.5	30.0	29.0
	r	0.9901	0.9932
	y-intercept	0.8857	0.8429
	slope	0.2713	0.2661

Relative response: 28% methane

CYCLOHEXANE

Total sample volume: 62 L

Trial No. 4

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	5.5	7.0	6.9
40	11.0	12.0	-
60	16.5	19.0	19.5
80	22.0	25.5	27.0
100	27.5	31.5	32.0
	r	0.9991	0.9992
	y-intercept	0.6429	0.8395
	slope	0.3071	0.3162

Relative response: 32% methane

ETHYL BENZENE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	1	1
20	6.2	14	12
40	12.4	23	20
60	18.7	42	35
80	24.9	47	41
100	31.1	51	49
	r	0.9788	0.9939
	y-intercept	3.3810	1.9000
	slope	0.5257	0.4886

Relative response: 51% methane

ETHYLENE DICHLORIDE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	1.2	1.2
20	4.1	9.0	10.0
40	8.2	17.0	18.0
60	12.2	28.0	29.0
80	16.3	48.0	46.0
100	20.4	58.0	56.0
	r	0.9863	0.9922
	y-intercept	-2.5619	-1.3714
	slope	0.5886	0.5614

Relative response: 55% methane

n-HEXANE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	2	2
20	6.6	12	12
40	13.3	23	23
60	19.9	33	32
80	26.5	44	43
100	33.2	57	55

r	0.9991	0.9993
y-intercept	1.2857	1.6190
slope	0.5443	0.5243

Relative response: 55% methane

n-HEXANE

Total sample volume: 62 L

Trial No. 2

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	6.6	10.5	10.0
40	13.3	17.5	17.0
60	19.9	24.0	24.5
80	26.5	33.0	34.0
100	33.2	40.0	40.0
	r	0.9987	0.9987
	y-intercept	1.7857	1.4762
	slope	0.3843	0.3921

Relative response: 40% methane

n-HEXANE

Total sample volume: 62 L

Trial No. 3

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	6.6	8.1	8.1
40	13.3	14.0	13.5
60	19.9	19.0	18.5
80	26.5	26.0	26.0
100	33.2	34.0	33.5
	r	0.9977	0.9974
	y-intercept	1.0381	0.9667
	slope	0.3196	0.3160

Relative response: 33% methane

METHANE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	1.2	1.2
20	2.1	2.8	2.7
40	4.1	4.9	4.9
60	6.2	6.9	6.9
80	8.2	8.7	8.6
100	10.3	10.2	10.0

	1st	2nd
r	0.9988	0.9973
y-intercept	1.1619	1.1667
slope	0.0924	0.0910

Relative response: 10% methane

METHYLENE CHLORIDE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	3.4	3.4
20	3.3	12.5	12.5
40	6.5	24	24
60	9.8	35	33
80	13.0	49	48
100	16.3	58.5	58
	r	0.9985	0.9976
	y-intercept	2.1143	2.0667
	slope	0.5657	0.5550

Relative response: 58% methane

METHYLENE CHLORIDE

Total sample volume: 62 L

Trial No. 2

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	3.3	11.0	12.0
40	6.5	21.0	21.0
60	9.8	31.0	32.0
80	13.0	42.5	42.0
100	16.3	50.5	50.0
	r	0.9994	0.9991
	y-intercept	1.0238	1.6190
	slope	0.5029	0.4943

Relative response: 51% methane

METHYLENE CHLORIDE

Total sample volume: 62 L

Trial No. 3

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	3.3	10.5	10.5
40	6.5	17.0	15.5
60	9.8	23.5	23.0
80	13.0	33.5	32.0
100	16.3	40.0	40.0
	r	0.9979	0.9974
	y-intercept	1.5952	1.2619
	slope	0.3864	0.3814

Relative response: 40% methane

2-METHOXY ETHANOL

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	3.2	3.2
20	4.0	5.3	5.2
40	8.0	7.9	7.8
60	12.0	10.0	9.9
80	16.0	10.0	10.0
100	20.0	12.0	11.0
	r	0.9763	0.9636
	y-intercept	3.7667	3.8857
	slope	0.0860	0.0793

Relative response 12% methane

METHYL ISOBUTYL KETONE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	6.0	6.0
20	6.3	14.0	15.0
40	12.6	26.0	26.0
60	18.8	35.0	35.0
80	25.1	49.0	48.0
100	31.4	60.0	60.0

	1st	2nd
r	0.9974	0.9980
y-intercept	4.2381	4.6667
slope	0.5486	0.5400

Relative response: 59% methane

MORPHOLINE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	5.7	5.7
20	4.4	8.5	8.0
40	8.8	13.0	11.0
60	13.3	19.0	18.0
80	17.7	22.5	22.0
100	22.1	28.0	27.5
	r	0.9958	0.9886
	y-intercept	4.7238	4.0810
	slope	0.2279	0.2257

Relative response: 27% methane

PROPYLENE OXIDE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	1	1
20	3.4	9.5	9.0
40	6.9	15.0	14.5
60	10.3	25.0	26.0
80	13.8	36.0	35.0
100	17.2	46.0	46.0
	r	0.9950	0.9950
	y-intercept	-0.3810	-0.5476
	slope	0.4493	0.4493

Relative response: 44% methane

TOLUENE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	1	1
20	5.4	9.5	10.5
40	10.4	30.0	26.5
60	16.2	51.0	39.0
80	21.6	75.0	65.0
100	27.0	87.5	73.0
	r	0.9930	0.9904
	y-intercept	-4.0952	-2.4524
	slope	0.9286	0.7657

Relative response: 81% methane

TOLUENE

Total sample volume: 62 L

Trial No. 2

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	5.4	12.5	9.0
40	10.4	27.0	16.0
60	16.2	37.0	21.0
80	21.6	57.0	45.0 - rej.
100	27.0	63.0	48.5

	1st	2nd
r	0.9942	0.9806
y-intercept	0.5238	-1.1757
slope	0.6479	0.4608

Relative response: 65% methane

*NOTE: Toluene dissolves the bag, cause to drastic decrease of R.R. from 1st to 2nd reading.

TOLUENE

Total sample volume: 62 L

Trial No. 3

ppm	µL	Reading 1st	Reading 2nd
0	0	1.0	1.0
20	5.4	10.5	6.6
40	10.4	18.5	10.0
60	16.2	29.0	-
80	21.6	40.0	30.0
100	27.0	50.0	41.5
	r	0.9989	0.9849
	y-intercept	0.2619	0.4077
	slope	0.4914	0.4077

Relative response: 49% methane

ORTHO-XYLENE

Total sample volume: 62 L

Trial No. 1

ppm	µL	Reading 1st	Reading 2nd
0	0	1	1
20	6.1	10.5	7.7
40	12.2	23.0	17.0
60	18.4	28.0	21.0
80	24.5	37.0	31.0
100	30.6	53.0	45.0
	r	0.9911	0.9872
	y-intercept	0.7048	-0.6476
	slope	0.4936	0.4213

Relative response: 51% methane

APPENDIX D

DATA FORMAT TO ENTER/EDIT DATA

```
CODE: (P)OINT (A)CQUISITION (D)ISPLAY (E)RASE (S)AVE (Q)UIT ?

CC=  XX  XX  XX  XX  XX  XX  XX  XXX

NN= NNNNN----------UP TO 50 CHARACTERS------------NNNNN NO=XXXX

FO= FFFFF----------UP TO 50 CHARACTERS------------FFFFF

MP= XXXXXX     XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

BP= XXXXXX     XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

DS= XX.XXX     XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

MW=XXXX.XX     XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

SC= A,T,#      XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

UN=            XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

SP=            XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

IN=            XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

MD=            XXXXX.XX   -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

CL=            XXXXX.XX   -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

GE=            XXXXX.XX   -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

ME=            XXXXX.XX   -1  -1  -1  -1  -1  -1  -1  -1  -1  -1
```

LEGEND:

BP - Boiling Point - -273 to 5000°C
CC - Compound Code - See coding method
CL - Cell path Length - 0 to 9999 millimeters
DS - DenSity - 0 to 32 g/cc
FA - FActor - 0.01 to 9.99
FO - FOrmula - up to 50 characters
GE - Gram Extinction coefficient - 0 to 3276.7
IN - INcrement of X-axis - -100 to 100
MD - MethoD 0 - 327.67 codes
ME - Molar Extinction coefficient 0 to 999999
MP - Melting Point - -273 to 5000°C
MW - Molecular Weight - 1 to 9999.99
NM - NaMe - up to 50 characters
NO - Number - 0 to 9999
SC - Scale of Y-axis - 0 to 1.00 Absorbance; 0-100% T; # 0-100
SP - Starting Point of X-axis - 0 to 4000
UN - UNit of X-axis - 1/CM, (M)icron, (MM)millimicron, (s)econd.

APPENDIX E

DATA ACQUISITION SYSTEM

Start computer system and select"SPECTROSCOPY AND ANALYSIS SYSTEM" from the program list or menu.

This in turn gives a menu or list of choises from which "DATAAQUI" is selected. This program will record sets of 120-data points per page whcih are displayed graphically on the screen for evaluation prior to proceeding to the transfer of the the 120 data points to the DATABASE.

Data acquisition is started and stopped by pressing any key on the computer keyboard. During the data acquisition the original data points are displayed on the screen at a rate of about 12 points a second. At the end of the data collection period the original data points are integrated to yield a data base of 120 data points and the original data is no longer available. If required, more than one page of data points may be recorded with a time delay in the experiment as is the case in recording an IR spectrum with a grating change at 2000 1/CM.

The data points are recorded and integrated to three significant figures for 0-999 by adjusting the instrument outpout voltage with a variable gain operational amplifier to set the voltage range at 0 to 5V. The significance of these digits must be related to the number of significant and reproducible figures of the experimental technique.

At the end of the data acquisition process the decision to record or the redo the experiment is elected by answering (N)O for redo and (Y)es to call the DATABASE program.

The program requires answers to:

IRF/UVF/SPF/GCF/MSF - select from IR, UV, Spectral Data, GC, MS formats.

(T)RANSFER/(L)OCAL/(C)ATALOG

- T to tranfer.
- L to tranfer 120 data points from DATAAQUI TO DATABASE.
- C to call the catalog of datacurves.

COMPOUND KEY NO. (XX,XX,XX,XX,XX,XX,XX,XXX)

- To identify each run by a selective numerical code. The seven two-digit codes can be grouped in two or more subgroups to indicate different types of information and the last three digit number as a library number for retrieval, e.g. 0,0,0,0,0,0,0,1

APPENDIX F

DATA FORMAT TO ENTER/EDIT DATA

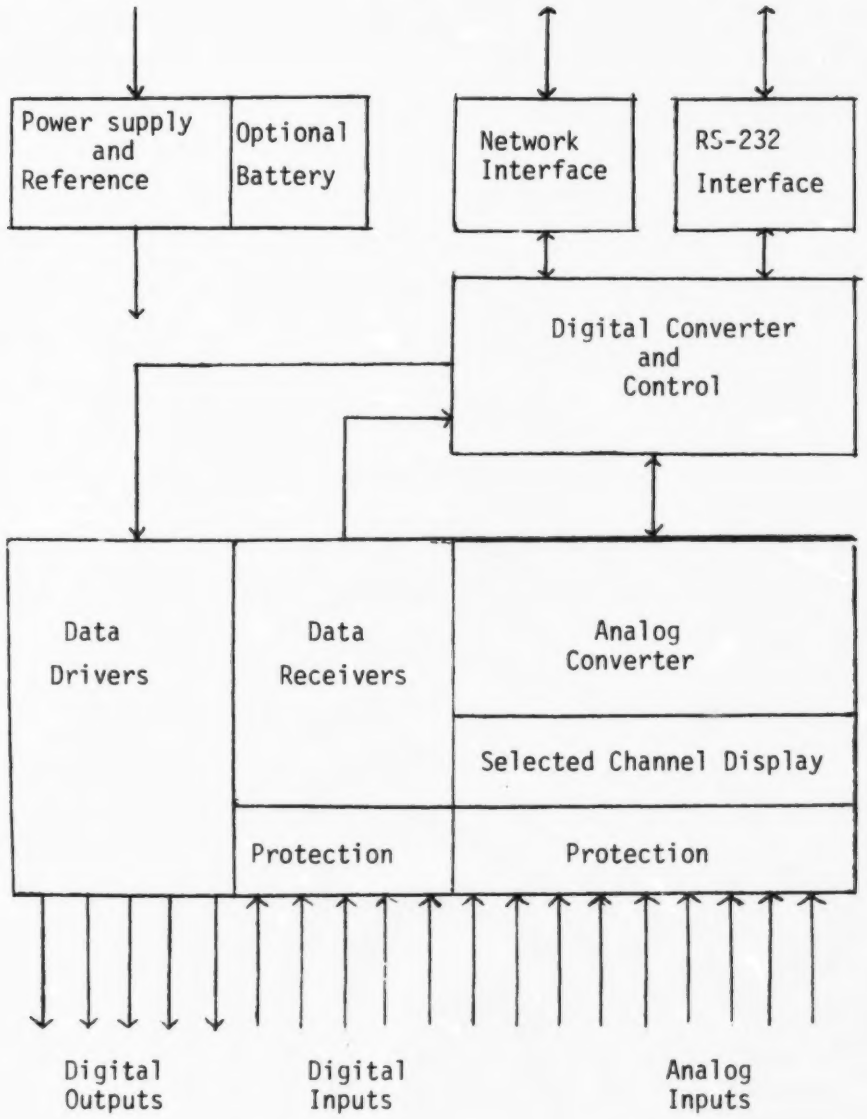
```
CODE: (P)OINT (A)CQUISITION (D)ISPLAY (E)RASE (S)AVE (Q)UIT ?

CC=  XX  XX  XX  XX  XX  XX  XX  XXX

NN= FFFFF----------UP TO 50 CHARACTERS------------NNNNN NO=XXXX

FO= FFFFF----------UP TO 50 CHARACTERS------------FFFFF

MP= XXXXXX     XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

BP= XXXXXX     XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

DS= XX.XXX     XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

MW=XXXX.XX     XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

SC= A,T,#      XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

UN=            XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

SP=            XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

IN=            XXXXX.X    -1  -1  -1  -1  -1  -,  -1  -1  -1  -1

IP=            XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

TL=            XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

GE=            XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1

DL=            XXXXX.X    -1  -1  -1  -1  -1  -1  -1  -1  -1  -1
```

LEGEND:

BP - Boiling Point - -273 to 5000°C
CC - Compound code - See coding method
DL - immediately Dangerous to Life or health
DS - DenSity - 0 to 32 g/cc
FA - FActor - 0.01 to 9.99
FO - FOrmula - up to 50 characters
GE - Gram - Extinction coefficient - 0 to 3276.7
IN - INcrement of X-axid - -100 to 100
IP - Ionization potential - 0 to 3276.7
MP - Melting Point - -273 to 5000°C
MW - Molecular Weight - 1 to 9999.99
NM - NaMe - up to 50 characters
NO - Number 0 to 9999
SC - SCale of Y-axis 0 to 1.00 Absorbance; 0-100%T, # 0 to 100
SP - Starting Point of X-axis - 0 to 4000
TV - Toxic limit Value - 1 to 9999
UN - Unit of X-axis - 1/CM, (M)icron, (MM)millimicron, (s)econd.

APPENDIX G

COMPUTER INTERFACE MODULE



APPENDIX H

COMPUTER STARTUP

1 - POWER SWITCH

Prior to switching the computer ON or OFF both diskette drives must be empty to avoid loosing information on the diskettes.

The POWER SWITCH is located at the right underside of the KEYBOARD. Turn the POWER SWITCH ON.

2 - Insert SYSTEM/PROGRAM diskette into the bottom drive (0) with the label facing UP and the read/write window pointing into the drive slot.

3 - Press RESET key (orange key) at the right of the keyboard. Then answer the following questions from the computer.

4 - Type: Month/Day/Year, e.g. XX/XX/XX followed by carriage return (CR).

5 - Type: Hour/Minute/second, e.g. XX/XX/XX (CR).

6 - The PROGRAM list or MENU will be displayed followed by a question mark.

(?) enter desired program.

APPENDIX I

DATABASE FORMAT

To edit the data pages type the appropriate code from the legend, and then enter the initial information or modify prior information. It is noted that data sets generated from the data acquisition system are assigned a compound key number prior to transfer to the database. Data sets entered in the edit mode must also be assigned a compound key number for subsequent recovery.

Descriptive information about a compound or mixture may be entered under the headings NaMe and FOrmula. Sequencing is provided by code NO.

When warranted, physical properties may be entered under Melting Point, Boiling Point, DenSity, Molecular Weight.

Optical parameters of Cell path Length, Gram Extinction and Molar Extinction coefficients may be recorded.

Methods for the above type of analysis my be coded under MD with numbers from 1 to 327.67.

Units of X-axis may be labelled as 1/CM, (M)icrons for IR and (MM) millimicrons for UV. For these and other techniques Starting Points of the X-axis may be selected in the region 0-4000 with increments of -100 to 100.

The FActor indicates the multiplier used to plot and printout on the Y-scale of 0 to 100 units scaled down to fit the resolution on the screen or plotter. The data in the database may have a resolution greater than on a in hundred depending on the resolution of the detectors and the accuracy of the analog to digital converter.

To enter data points manually or edit individual data points enter P and number of datum point 1 to 120 (in 12 rows of 10 data points) followed by the specific datum. If it is required to repeat a number n times for n data points the the number followed ny -n, e.g. 0, -7.

ULTRAVIOLET-VISIBLE SPECTROPHOTOMETRIC ANALYSIS OF GASES AND VAPORS

Open the sample compartment cover and replace the front standard 1-cm cuvette holder (most frequently used) with the special gas cell holder supplied. The gas cell is then inserted in the sample beam.

The back cuvette holder in the reference beam is not used and may remain in position or may be removed.

The gas cell holder must be aligned with the two aligning screws from the standard cuvette holder for proper positioning. When the gas cell holder is no longer required, replace the standard cell holder and return the aligning screws to their initial position.

Flush the gas cell with a stream of pure nitrogen gas from from a cylinder supplied. Then set the gas cell in the gas cell holder only after the POWER SWITCH is turned ON and the MICROCOMPUTER conditiones the instrument with standard checks and set initial parameters. This procedure is completed when the instrument has scanned through the full wavelength region from 750 to 190 nanometers.

Then turn ON the UV deuterium lamp for the wavelength region of 190 to 315 nm and/or the VISIBLE tungsten-bromide lamp for the wavelength region 315 to 750 nm.

Zero the absorbance for the nitrogen flushed gas cell at the wavelength with the highest absorption in the ragion to be studied. For the 190 to 315 nm range and quartz cell windows this is normally done at the gighest wavelength to be scanned. If only the range of 290 to 190 nm is to be scanned this is done at 290 nm.

Introduce 10 microliters or 0.01ml. to determine the vapor spectra of liquids or liquid mixtures in the gas cell and plug the inlets with teflon plugs.

Set the instrument parameters as required by the type of spectrum to be recorded within the parameter ranges suggested by the manufacturer.

For more details see Procedure to Record Gas/Vapor Spectra.

APPENDIX J

PROCEDURE to RECORD ULTRAVIOLET-VISIBLE GAS/VAPOR SPECTRA

Select the absorbance range or ranges to be used, e.g. 0.0 to 1.0A with readability of 0.01A units on a standard recorder chart for low absorbance wavelength regions and 0.0 to 3.0 for very strong absorbance wavelength regions with 0.03A readability. For very low absorbance wavelength ranges scales of 0.0 to 0.5 or lower may be used.

To obtain a readability of 0.01A for absorbances in the range of 1.0 to 2.0A is is required to zero at absorance 1.0 with the AUTO ZERO KEY and then key in the 1.0 to 2.0 absorbance limits. Note peak absorbance in the range -0.300 to 3.000 may be read to 0.002A repeatability and an accuracy of 0.005A on the ORDINATE DISPLAY.

To set the lower absorbance range limit first enter the numerical value on the KEYBOARD and then press the ORD MIN KEY. To set the upper absorbance range limit first enter the numerical value on the KEYBOARD and then press the ORD MAX KEY.

Following the setting of the absorbance limits set the upper wavelength limit by entering the upper numerical value in nanometers and press the MAX KEY. The lower limit is automatically set at 190 nm. If it necessary to scan to a λMIN greater than 190 nm first set the λMAX and go to λMAX, then enter the lower λ value in nanometers and press the λMIN KEY.

For gases or vapors set SLIT WIDTH at 0.25 nm with SLIT SELECTOR, SCAN SPEED at 20 nm/min with SCAN SPEED KEY, RESPONSE TIME at 0.5 sec. with RESPONSE KEY, ABSORBANCE with the MODE KEY. Set RECORDER SPEED at 4 cm/min to give a readability of 0.5 NANOMETERS (or smaller easily read values). For maximum quantitative accuracy scan over the required absorbance maxima at a SCAN SPEED of 5 nm/min to determine extinction coefficients and percent composition of mixtures.

For maximum wavelength and absorbance accuracy it is required to read the ABSCISSA DISPLAY and the ORDINATE DISPLAY at a specified wavelength. This can be achieved by scanning with the λFWD KKEY and the λREV KEY. The λFWD KEY causes the wavelength to be scanned from high to low nanometers at an initial rate of 5 nm/min for 5 seconds, then at 20 nm/min for the next 5 seconds and then at a maximum speed of 480 nm/min. The λREV KEY operates as the λFWD KEY with a scan from low to high nanometers. By using both thes KEYS it is possible to zero in on a specific wavelength to a theoretical limit of 0.1 nanometers and read the absorbance to a theoretical limit of 0.001A units.

APPENDIX K

INFRARED SPECTROPHOTOMETRIC ANALYSIS OF GASES AND VAPORS

Slide the sample compartment cover to the right and insert the special gas cell holder in the mounting bracket of the front sample beam. Flush the gas cell with a stream of pure nitrogen gas from a supplied cylinder. Then set the gas cell on the supporting rods aligned in the sample beam. If correctly aligned the NaCl windows will yield an absorbance of 1.00 at around 550 wavenumbers. If improperly aligned the absorbance maxima will be less than 1.00.

Turn ON the POWER SWITCH and allow the microprocessor to carry out the initial checks ending by 4000 1/CM on the ABSCISSA display.

Set the absorbance at approximately 0.15A units at 4000 1/CM with the OFFSET Control after depressing the ORDINATE EXPANSION button with the BASELINE Control turned to its upper maximum. Then run a baseline as in Spectrum 2 in Procedure to Record Gas/Vapor Spectra.

Carefully remove the left teflon plug from the gas cell in the sample compartment without interfering with the gas cell alignment in the sample beam.

Introduce 10 ul or 0.01 ml of the liquid to determine the vapor spectrum of a pure liquid or a mixture in the gas cell and plug the inlets with the teflon stoppers.

Set the instrument parameters as required by the type of spectrum to be recorded within the limits suggested by the manufacturer.

For more details see Procedure to Record Infrared Gas/Vapor Spectra.

APPENDIX L

PROCEDURE TO RECORD INFRARED GAS/VAPOR SPECTRA

Set POWER SWITCH, at bottom, front right side of the instrument to ON. The microprocessor will proceed with the required checks and end with 4000 wavenumbers on the ABSCISSA display. Set:

SCAN TIME to NORMAL by depressing the black button,
MULTIPLIER to 1 by depressing the black button,
CHART EXPANSION to 0.5 by depressing the 0.5 button

For gas/vapor spectra it is advisable to compensate for the gas cell windows aperture and absorbance as well as sligth variations in the cell positioning with the OFFSET Control. This control is an electrical signal attenuator rather than a mechanical beam attenuator at its ORDINATE EXPANSION setting of 100. Spectra 1 shows the baseline spectrum of the gas cell and the spectrum of Chlorobenzene recorded with a beam attenuator. Spectrum 2 is run with OFFSET Control for Chlorobenzene and is fully superimposable on spectrum 1. The OFFSET Control is activated by depressing the ORDINATE EXPANSION button as indicated by the red light. The ORD EXP feature allows the expansion of any spectrum or part thereof to near full chart for better readability or better evaluation of weak features such as the substitution patterns of the benzene ring.

The maximum absorbance range of the instrument is 0.00 to 1.00A. The ORD EXP allows the expansion of any fraction of the ordinate from 0.10A to 1.00A to full scale with the ORD EXP settings of 010 to 100. It is to be noted that if the baseline is not flat as shown in spectrum 2 (between 0.05A to 1.4A units) it would vary by the same expansion factor as the sample absorption as shown in spectrum 3, where expansion 100 yields a variation of 0.10 (0.17 - 0.07) and for 200 a variation of 0.20 (0.21 - 0.01) absorbance units.

The absorbance range of 0.00 to 1.00A may be compressed by any factor from 0.10 to 1.00 to yields spectra sized of 1.5 cm by 28(56)cm to 15 cm by 28(56) cm.

The following are typical settings for Gas/Vapor Spectra.

SPECTRA	SCAN TIME	SLIT	MULT.	NOISE	CHART	ORD EXP	MODE
Baseline	3	WIDE	X1	1	0.5	100	A
Survey	6	WIDE	X1	1	0.5	100	A
Qualitative	12	NORMAL	X1	1	0.5	100-999	A
Quantitative	6	WIDE	X1	X ½	0.5	100	A

APPENDIX M

INFRARED SPECTRAL PATTERN RECOGNITION SYSTEMS - IRBASIC & IRPAT

The IRBASIC system is a computer data base of IR vapor spectra of the typical spectra of the frequently encountered functional groups as listed in TABLE II. The IRPAT system is a computer data base of 360 plus spectra of liquid and solid mono, di and trifunctional-group compounds.

A short list of chemical groups based on chemical tests and a preliminary interpretation of the IR spectrum is required for the search program to generate effectively a limited number of typical patterns.

The system generates a limited number of patterns from specific compounds described by three word phrases. The first phrase - a group of words that form a sense unit - is the qualifier of the second phrase. The second phrase defines a one, two, three or four-functional compound. The last word of the first phrase may be used to describe a fifth functional group present.

The numerical codes for qualifiers are given in TABLE I and those for the functional groups in TABLE II. A simple coding method was selected to coordinate the chemical functional groups into logical sections. In general the sections correspond to chemical affinity groups for chemical activity groups as described below.

01 - 10 Acidic compounds.

11 - 20 Basic compounds and compounds reducible to bases.

21 - 30 Salts of all types, hydrates, etc.

31 - 40 Alcohols, mercaptans, carbonyls, carbohydrates and polyols.

41 - 50 Ethers, sulfides, acetals, orthoesters, anhydrides, acid halides, sulfonyl halides and peroxides.

51 - 60 Esters, lactones, sulfonates, sulfones, sulfoxides, esteramides, amides, lactam, sulfonamides.

61 - 69 Ureas, thioureas, sulfoamides, thioamides, cyanates, isocyanates, thiocyanates, isothiocyanates, diimides, nitroes nitrosoes, amine oxides, nitrites, nitrates and substituted imides.

70 - 80 Hydrocarbons and halides.

81 - 86 Compounds with other elements (excluding salts) and mixtures.

Coding Rules for IRBASIC & IRPAT

A three-phrase paragraph is used to code each IR spectrum. Of the eight numerical codes in the paragraph, the first three constitute the qualifier phrase; the next four the functional group phrase; and the eight one the library phrase. When more than four functional groups are present the last word of the first phrase must be used to describe it. The qualifier codes are listed in TABLE I, the functional codes in TABLE II and the library codes are either sequential numbers or the molecular weight of the compound to retrieve patterns in a prearranged order. The use of numerical codes is illustrated with the following benzoic acid compounds.

The codes for 3-METHOXY-BENZOIC ACID are:

Qualifiers			Functional Groups				Sequence
00	03	00	00	78	41	01	01

The codes for 3-METHOXY-2-HYDROXYBENZOIC ACID are:

Qualifiers			Functional Groups				Sequence
03	02	00	78	41	05	01	01

The four numerical codes in the functional phrase are most frequently, if not always, in decreasing order, e.g. 00784101 and 78410501.

In the qualifier phrase the codes are listed in the order and position to refer directly to the last three functional groups they qualify. In the second example the 03 refers to 41, which stands for methoxyether, and 02 refers to 05, which stands for phenolic OH.

In polycyclic and heterocyclic compounds ring number systems must be known and each functional group position must be numbered.

When coding a functional group which results from the reaction of to other functional groups such as ester, amides, etc. it is necessary to indicate the type of acid and alcohol or amine, etc. from which the ester, amide, etc. originated. This is shown with alkyl 70 and C6H5 78.

Ester from:	ROH and RCOOH	00	00	00	00	00	00	51	00
	ROH and ARCOOH	00	00	00	00	70	78	51	00
	AROH and RCOOH	00	00	00	00	78	70	51	00
	AROH and ARCOOH	00	00	00	00	78	78	51	00
Amides from:	RRNH and RCOX	00	00	00	00	00	00	57	00
	RARNH and RCOX	41	00	00	78	70	70	57	00
	ARARNH and RCOX	42	00	00	00	78	70	57	00
	RRNH and ARCOX	00	00	00	00	70	78	57	00
	RARNH and ARCOX	41	00	00	78	70	78	57	00
	ARARNH and ARCOX	42	00	00	00	78	78	57	00
Ethers from:	ROH and ROH	00	00	00	00	00	00	41	00
	ROH and AROH	00	41	00	00	00	78	41	00
	AROH and AROH	00	42	00	00	00	78	41	00

Applications of the INFRARED PATTERN RECOGNITION SYSTEMS

The IRBASIC and IRPAT systems are available on all terminals of the Concordia University Computer Center. Obtain LOG IN procedure from the Chemistry Department.

When the program is accessed it is strongly advised to request specific patterns to verify preliminary conclusions resulting from the chemical and physical tests performed and the IR and UV spectra obtained.

For acidic compounds, as an example, it is most useful to determine the degree of acidity and the presence of other elements such as N, S, or X. A boiling point or melting point, even is only approximate, will be usefull in the sequential search for corresponding acid models. When extensive hydrogen bonding is indicated by very broad hydroxy bands; then amino, hydroxy,hydrates or polyacids are indicated. Extensive hydrogen bonding in neutral compounds on the other hand would indicate polyhydroxy compounds, amino alcohols, hydrated salts, etc.

The UV spectra of weak aromatic acids and bases vary markedly from acidic, to neutral to basic solutions.

The above information and a variety of other pertinent information allows to start the search with specific combinations such as:

-9	-9	-9	-9	-9	78	01	-9	for aromatic acids
-9	-9	-9	-9	-9	74	01	-9	for chloro acids
-9	-9	-9	-9	-9	11	01	-9	for primary amine-acids
-9	-9	-9	-9	-9	12	01	-9	for secondary amine-acids
-9	-9	-9	-9	-9	14	01	-9	for tertiary amine-acids

where -9 is the code for no data available for these words. Then we can proceed through a limited number of specific patterns for each type of acids. If this procedure is not followed it might be required to proceed sequentially through 20 or more acid models, trying to remember the model that best fits the spectrum under study.

It is highly advisable to try to retrieve from a data base only the information that is directly applicable to the problem under study. If this logic is followed, the computer search will assist the investigator in arriving as a better solution in the minimum time rather than confuse him with an excessive amount of random information. It must be realized that the computer program is not a substitute to the investigator's

logical and imaginative approach to a problem; but a most effective and rapid method to retrieve selected information to zero in on the best answer to a problem.

The analysis of neutral compounds in general will require more information on the presence of O, N, S or X and some indication of the most significant IR bands and any absorbance in the UV spectrum. For example, a ketoester would require the identification of the keto and ester C=O bands in the infrared. If such an ester is indicated from the physical properties of the compound it would require comparing the sample's IR spectrum with the IR spectra of an ester and a ketoester as:

```
-9  -9  -9  -9  -9  51  -9   for simple esters
-9  -9  -9  -9  51  37  -9   for ketoesters
```

A printout of the relevant information in the IRPAT data base with the three phrases, names and formulas of the 360 plus compounds is available in the laboratory for consultation. The list consists of:

66 monofunctional compounds
117 difunctional compounds
140 trifunctional compounds
37 tetrafunctional compounds

This listing illustrates that the codes in the second phrase are generally listed in the order that will generate the largest number, as mentioned in the coding rules, but not necessarily so, given that 116 out of 117 difunctional compounds and 120 out of 140 trifunctional compounds and 27 out of 37 tetrafunctional compounds do follow the rule. In the remaining 31 cases it can readily be seen that the two codes of the second phrase must be inverted to exactly describe the compound.

Normally it is not required to search with the qualifier phrase unless a very specific type of compound is required. This necessitates a more detailed knowledge of the coding interactions between the qualifier terms and the functional terms. The seven most descriptive codes must be selected since for ease of operation the qualifier and functional phrases must be limited to three words and four words respectively.

For very complex molecules, with more than four functional groups, it may be required to code a functional group with the third word of the qualifier phrase. The functional group codes 70 to 77 may be used in this fashion without any possibility of error, since these codes as qualifiers are not related to chemical structure.

The codes 78 to 86 have the same meaning as qualifier or functional codes. The codes 92 to 99 are used in the same manner.

The codes 92 to 99 are most frequently used in general searches for cyclic compounds and heterocyclic compounds. In the IRPAT data base these codes are used 39 times in the functional group phrase.

11 times as the first word of the functional group phrase
17 times as the second word of the functional group phrase
11 times as the third word of the functional group phrase

The qualifier phrase is readily constructed in searches for very specific types of compounds like diacids, diesters or diphenylamines.

diacid	-9	-9	42	-9	-9	-9	01	-9	for 1 hit
diesters	-9	-9	42	-9	-9	-9	51	-9	for 2 hits
diphenylamines	-9	42	-9	-9	-9	78	11	-9	for 1 hit

To distinguish between aldo and keto hexoses it is required to search for a pentahydroxy aldehydic sugar and pentahydroxy ketonic sugar as follows:

aldohexoses	-9	45	-9	-9	-9	40	36	-9	for 1 hit
ketohexoses	-9	45	-9	-9	-9	40	37	-9	for 1 hit

To distinguish between the three nitrophenol isomers the three required searches are:

2-nitrophenol	-9	02	-9	-9	78	65	05	-9	no hit
3-nitrophenol	-9	03	-9	-9	78	65	05	-9	for 1 hit
4-nitrophenol	-9	04	-9	-9	78	65	05	-9	for 1 hit

the no hit for 2-Nitrophenol is an indication that this compound is not listed in the data base.

For more detailed information the reader is again referred to the printout of the relevant information in the IRBASIC and IRPAT data bases with their three phrases, names and formulas available in the laboratory for consultation.

In the IRBASIC, IRF and UVF data bases where the molecular weight of the compound is used as the word in the library phrase, it is required to distinguish between different isomers with the same moleculr weight. This is achieved by using the codes -1 to -9 as the third word of the qualifier phrase. This is illustrated with the following three isomeric esters: propyl formate, ethyl acetate and methyl propionate.

HCOOC3H7	00	00	-1	00	00	00	51	88	propyl formate
CH3COOC2H5	00	00	-2	00	00	00	51	88	ethyl acetate
C2H5COOCH3	00	00	-3	00	00	00	51	88	methyl propionate

Note that isopropyl formate would be coded differently as

HCOOCH(CH3)2	00	00	87	00	00	00	51	88	isopropyl formate

TABLE I - QUALIFIER CODES

Position Codes

1 - 1
2 - 2
3 - 3
4 - 4
5 - 5
6 - 6
7 - 7
8 - 8
9 - 9
10 - 10
11 - 1.1
12 - 1,2
13 - 1,3
14 - 1,4
15 - 1,5
16 - 1,6
17 - 1,7
18 - 1,8
19 - 1,2,3
20 - 1,2,4
21 - 1,3,5
2,4,6
22 - 1.2.3.4
23 - 2,3
24 - 2,4
25 - 2,5
26 - 2,6
27 - 2,7
28 - 2,8
29 - 2,9
30 - 3,5

Type Codes

31 - ALPHA
32 - BETA
33 - GAMMA
34 - DELTA
35 - EPSILON
36 - N-Substituted
37 - MONO-Substituted
38 - DI - "
39 - TRI - "
40 - POLY- "
41 - MONO
42 - DI
43 - TRI
44 - TETRA
45 - PENTA
46 - HEXA
47 - HEPTA
48 - OCTA
49 - NONA
50 - DECA

Spectroscopic Methods

51 - Gas - 10-cm or specified
52 - Liquid film specified
53 - Capillary neat
54 - Capillary melt
55 - Cast film - sublimate
56 - KBr disc
57 - KI/CsI disc or cell
58 - Mull - nujol
59 - Mull - fluorolube
60 - ATR
61 - CS2 solution
62 - CHC13 "
63 - CC14 "
64 - CC12=CC12 "
65 - CH3NO2 "
66 - THFURAN "
67 - C6H6 solution
68 - HYDROCARBON "
69 - C6H5C1 "
70 - DIOXANE "
71 - CH3OH, C2H5OH "
72 - CH3OH.HC1 "
73 - CH3OH.NaOH "
74 - H2O "
75 - H2O.HC1 "
76 - H2O.NaOH "
77 - OTHER

Functional Codes

78 - Phenyl
79 - Naphthyl
80 - Aromatic
81 - Si compounds
82 - P compounds
83 -
84 -
85 -
86 - Mixtures

Structure Codes

87 - ISO
88 - SEC
89 - TERT
90 - CIS
91 - TRANS
92 - MONO CYCLIC
93 - DI "
94 - TRI "
95 - POLY "
96 - MONOHETEROCYCLIC
97 - DI "
98 - TRI "
99 - TETRA "

TABLE II - FUNCTIONAL GROUP CODES

1. -CO-OH - Carboxylic acids
2. $-SO_2-OH$ - Sulfonic acids
3. -SO-OH - Sulfinic acids
4. -CO(O)-OH - Peroxyacids
5. AROH - Phenols
6. -CS-OH - 01 Thioacids
   -CO-SH - 21 "
   -CS-SH - 41 "
7. AR-SH - Thiophenols
8. -HC=N-OH - 01 Oximes
   -RC=N-OH - 31 "
   -CO-NH-OH - 61 Hydroxamic acids
9. -CO-NH-CO- - Imides
10. $-NH-SO_2-OH$ - Sulfamic acids
11. $-NH_2$ - Primary amines
12. -NH- - Secondary amines
13. -NH- - " " cyclic
14. -N= - Tertiary amines
15. -N= - " " cyclic
16. $-NH-NH_2$ - Hydrazines
17. -N=CH- - 01 Amine azines
    -HC=N-N=CH- - 21 Hydrazine azines
    -NH-N=NH - 41 Amidines
18. -N=N- - 01 Azoes
    -NH-NH- 21 Hydrazoes
    -NH-N=NH- - 41 Triazines
19. -C=-N - 01 Nitriles
    -N=C 81 Isonitriles
20. -NH-N=CH- 01 Hydrazones
    -NH-N=C= 31 "
    -NH-CO-NH-N=CH- 61 Semi-
    -NH-CO-NH-N=C= 71 - carbazones
    -NH-CS-NH-N=CH- 81 Thio-
    -NH-CS-NH-N=C= 91 - carbazones
21. -CO-O- - Carboxylate salts
22. $-SO_2-O-$ - 01 Sulfonate salts
    $-O-SO_2-O-$ - 81 Sulfate salts
23. -SO-O- - 01 Sulfonite salts
    -O-SO-O- - 81 Sulfite salts
24. Ar-O- - 01 Phenol salts
    $(-O-CO-)_2N-$ - 51 Imide salts
25. $-NH_2.HX$ - 01 Prim. Amine salts
    -NH-.HX - 21 Sec. Amine salts
    -NH-.HX - 41 Cyclic Amine salts
    =N-.HX - 61 Tert. Amine salts
    =N-.HX - 81 Cyclic Amine salts
26. $NH_3.HX$ - 01 Ammonium salts
    $NH_2-NH_2.HX$ - 51 Hydrazine salts
27. RxNHy.A - 01 Amine-acid salts
    RxNHy.OAR - 51 Phenol-amine salts
28. RxNHy.RX - 01 Quaternary salts
    $RxNHy.RSO_2R$ - 51 Quaternary salts
29. $\cdot(H_2O)_n$ - Hydrates
30. Hydroxy - Others
31. $-CH_2-OH$ - Primary alcohols
32. -CHR-OH - Secondary alcohols
33. -CRR-OH - Tertiary alcohols
34. -CHOH- - Cyclic alcohols
35. -SH - Mercaptans
36. -CHO - Aldehydes
37. -CO- - Ketones
38. -CO- - 01 Cyclic ketones
    -CO- - 51 " diketones
39. Carbohydrates
40. $-(CHOH)_x$ - Polyols
41. -O- - Ethers
42. -O- - Cyclic ethers
43. -S- - Sulfides

TABLE II - FUNCTIONAL GROUP CODES

44. -S- - Cyclic Sulfides
45. -S-S- - Disulfides
46. $-CH(OR)_2$ - 01 Acetals
    $-C(OR)_2-$ - 31 Cyclic acetals
    $-C(OR)_3$ - 61 Orthoesters
47. -OC-O-CO- - Anhydrides
48. -CO-X - Acid halides
49. $-SO_2-X$ - Sulfonyl halides
50. -O-O- - Peroxides
51. -CO-OR - 01 Esters
    -CO-O- - 51 " cyclic lactones
52. $-SO_2-OR$ - Sulfonates
53. $-SO_2-$ - 01 Sulfones
    -SO- - 51 Sulfoxides
54. $-O-CO-NH_2$ - 01 esteramide-urethane
    -O-CO-NH- - 31 "
    -O-CO-N= - 61 "
55. $-CO-NH_2$ - 01 Amides of NH_3
    $-CO-NH-NH_2$ - 81 " of NH_2-NH_2
56. $-CO-NH-$ - 01 Amides of $-NH_2$
    -CO-NH- - 81 Cyclic amides, lactam
    -CO-NH- - 91 Amides of $-NH-NH_2$
57. -CO-N= - Amides of =NH
58. $-SO_2NH_2$ - Sulfonamide of NH_3
59. $-SO_2NH-$ - Sulfonamide of $-NH_2$
60. $-SO_2N=$ - Sulfonamide of =NH
61. -HN-CO-NH- - 01 Ureas
    -HN-CS-NH- - 31 Thioureas
    $-NH-SO_2-NH-$ - 61 Sulfoamides
62. $-CS-NH_2$ - Thioamides
63. -O-C=-N - 01 Cyanates
    -N=C=O - 21 Isocyanates
    -S-C=-N - 41 Thiocyanates
    -N=C=S - 61 Isothiocyanates
    -N=C=N- - 81 Diimides
65. $-NO_2$ - Nitroes
66. -NO - 01 C-nitrosoes
    R_3NO - 81 Amine oxides
67. =N-NO - N-nitrosoes
68. -O-NO - 01 Nitrites
    $-O-NO_2$ - 51 Nitrates
69. -CO-NR-CO- Substituted imides
70. $-CH_2-$ - Alkanes
71. $-CH=CH_2$ - Alkenes
72. -C=-CH - Alkynes
73. -F - Fluoro
74. -Cl - Chloro
75. -Br - Bromo
76. -I - Iodo
77. Cycloalkanes, cycloalkenes
78. $-C_6H_5$ - Phenyl
79. $-C_{10}H_7$ - Naphthyl
80. Other Aromatic Hydrocarbons
81. Si compounds
82. P compounds
83.
84.
85.
86. Mixtures